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(54) Title: CARBON DIOXIDE-PHILIC COMPOUNDS AND METHODS OF SYNTHESIS THEREOF

(57) Abstract: A method of synthesizing a CO_2-philic analog of a CO_2-phobic compound, includes the step of: reacting the CO_2-pho-
bic compound with a CO_2-philic compound selected from the group of a polyether substituted with at least one side group including
preferably a Lewis base, a polycarbonate, a polycarbonate substituted with at least one side group including preferably a Lewis base,
a vinyl polymer substituted with at least one side group including preferably a Lewis base a poly(ether-ester) or a poly(ether-ester)
substituted with at least one side group including preferably a Lewis base, to create the CO_2-philic analog. A method of synthesizing
a CO_2-phile includes the step of copolymerizing at least two monomers, wherein a polymer formed from homopolymerization of
one of the monomers has a T_g of less than approximately 250 K and a steric factor less than approximately 1.8, at least one of the
monomers contains a group that results in a pendant group from the CO_2-phile backbone that contains a Lewis base group, and the
resultant CO_2-phile does not contain both hydrogen bond donors and acceptors.
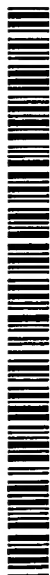
CARBON DIOXIDE-PHILIC COMPOUNDS AND
METHODS OF SYNTHESIS THEREOF

Related Application

5   The present application is related to United
States Provisional Patent Application Serial No. 60/155,960,
filed September 24, 1999, assigned to the assignee hereof,
the disclosure of which is incorporated herein by reference.

Field of the Invention

10   The present invention relates to compounds that
are soluble in or miscible in carbon dioxide and to methods
of synthesizing such compounds.

Background of the Invention

          Various publications are referenced herein to, for
15 example, clarify the general state of the art. Reference to
a   publication   herein   is   not   an   admission   that   the
publication is prior art or relevant to the patentability of
the present invention.

          The feasibility of using carbon dioxide or CO_2 as
20 a process solvent has been extensively investigated in both
academic and industrial circles because CO_2 is considered to

be an environmentally benign solvent. Previous solubility parameter calculations using equation of state information suggested that the solvent power of CO_2 was similar to that of short n-alkanes, leading to hopes that CO_2 could replace

5   a wide variety of non-polar organic solvents. King, J.W., Poly. Mat. Sci. Eng. Prepr. (1984), 51, 707. Although such solubility parameter values precluded the use of CO_2 for processing of polar or hydrophilic materials, it was believed that addition of conventional alkyl-functional

10 surfactants could effectively deal with the problem. However, early attempts to employ conventional surfactants in CO_2 failed as a result of the poor solubility of the amphiphiles, despite the fact that these same molecules exhibited adequate solubility in ethane and propane.

15 Consani, K.A.; Smith, R.D.; J. Supercrit. Fl. (1990), 3, 51. It was later discovered that the early solubility parameter calculations, while mathematically correct, failed to note that the absolute value was inflated by as much as 20% by the strong quadropole moment of CO_2 (which also inflates its

20 critical pressure). Myers, A.L.; Prausnitz, J.M., Ind. Eng. Chem. Fundam. (1965), 4, 209.

        Johnston   and   colleagues   suggested polarizability/volume as a better quantity by which to judge solvent power. O'Shea, K.; Kirmse, K.; Fox, M.A.; Johnston,

25 K.P.; J. Phys. Chem. (1991), 95, 7863 (b) McFann, G.J.; Howdle, S.M.; Johnston, K.P.; AIChE J. (1994), 40, 543 (c) Johnston, K.P.; Lemert, R.M.; in Encyclopedia of Chemical Processing and Design, McKetta, J.J., Ed; Marcel Dekker: New York (1996), 1. On the basis of polarizability/volume, CO_2

30 is a poor solvent compared to short n-alkanes. As the 1980's drew to a close, a number of research groups began to explore the design of CO_2-philic materials, (that is,

compounds which dissolve in or are miscible in CO_2 at significantly lower pressures than alkyl functional analogs). For example, Harrison et al. generated a hybrid alkyl/fluoroalkyl surfactant that both dissolved in CO_2 and
5   solubilized significant amounts of water. Harrison, K.; Goveas, J.; Johnston, K.P.; O'Rear, E.A.; Langmuir (1994), 10, 3536. DeSimone and coworkers generated homo- and copolymers of fluorinated acrylates which exhibit complete miscibility with CO_2 at moderate pressures. DeSimone, J.M.;
10   Guan, Z.; Elsbernd, C.S.; Science (1992), 257, 945. Block copolymers featuring fluorinated acrylate monomers were used to support dispersion polymerization in CO_2, allowing generation of micron-size monodisperse spheres. Hsiao, Y.L.; Maury, E.E.; DeSimone, J.M.; Mawson, S.M.; Johnston,
15   K.P.; Macromolecules (1995), 28, 8159. Fluoroether-functional amphiphiles have been used to support emulsion polymerization as described in Adamsky, F.A.; Beckman, E.J.; Macromolecules (1994), 27, 312, solubilize proteins as described in (a) Ghenciu, E.; Russell, A.J.; Beckman, E.J.;
20   Biotech. Bioeng (1998), 58, 572 (b) Ghenciu, E.; Beckman, E.J.; Industr. Eng. Chem. Res. (1997), 36, 5366; and Johnston, K.P.; Harrison, K.L.; Clarke, M.J.; Howdle, S.; Heitz, M.P.; Bright, F.V.; Carlier, C. Randolph, T.W.; Science (1996), 271, 624, and extract heavy metals from soil
25   and water as described in (Yazdi, A.V.; Beckman, E.J.; Ind. Eng. Chem. (1997), 36, 2368; and Li, J.; Beckman, E.J.; Industr. Eng. Chem. Res. (1998), 37, 4768.

        In general, compounds not soluble or miscible in CO_2 (that is, CO_2-phobic compounds) can be made soluble or
30   miscible in CO_2 by synthesizing analogs of such compounds incorporating one or more CO_2-philic groups. Processes and reactions that are normally not possible in CO_2, are thereby

made possible. For example, surfactants, chelating agents and reactants for use in carbon dioxide can be synthesized in this manner. CO_2-phobic compounds that can be modified with CO_2-philic groups to create CO_2-philic analogs for

5   processing in CO_2 are disclosed, for example, in U.S. Patent Application Serial No. 09/106,480, entitled Synthesis of Hydrogen Peroxide and filed June 29, 1998, the disclosure of which is incorporated herein by reference, in which hydrogen peroxide is synthesized in CO_2 using a CO_2-philic

10   functionalized anthraquinone reactant. Moreover, CO_2-philic chelating agents for extraction of metals in carbon dioxide are disclosed U.S. Patent No. 5,641,887 and U.S. Patent No. 5,872,257, the disclosures of which are incorporated herein by reference. Other CO_2-philic functionalized

15   compounds are disclosed in U.S. Patent No. 5,589.105, U.S. Patent No. 5,789,505, U.S. Patent No. 5,639,836, U.S. Patent No. 5,679,737, U.S. Patent No. 5,733,964, U.S. Patent No. 5,780,553, U.S. Patent No. 5,858,022, U.S. Patent No. 5,676,705, U.S. Patent No. 5,683,977, and U.S. Patent

20   No. 5,683,473, the disclosures of which are incorporated herein by reference.

It has been theorized that only molecules with very low solubility parameters (that is, fluorine-containing and silicon-containing molecules) are sufficiently

25   CO_2-philic to synthesize CO_2-philic analogs or amphiphiles suitable for commercial processing in CO_2. O'Neill, M.L.; Cao, Q.; Fang, M.; Johnston, K.P.; Wilkinson, S.P.; Smith, C.D.; Kerschner, J.L.; Jureller, S.H.; Ind. Eng. Chem. Res. (1998), 37, 3067. Indeed, it is the common belief in the

30   art that only fluorine-containing and silicon-containing molecules are viable solutions in synthesizing commercially viable CO_2-philic analogs. The most successful CO_2-philic

modifiers or moieties to date are fluorinated compounds. Despite success in development of fluorinated and silicon-containing CO_2-philic amphiphiles, the cost (on a mass basis) of these materials (typically, on the order of $1/gram) renders the economics of a process unfavorable unless the amphiphile can be efficiently recycled. Whereas in-process recycling of a "CO_2-phile" may at times be straightforward, this is not true in all cases where CO_2 has been proposed as a replacement for organic solvents.

It is very desirable to develop CO_2-philic compounds or CO_2-philes that are effectively soluble in or miscible in CO_2 while being relatively inexpensive to synthesize and use.


Summary of the Invention

The present invention provides, generally, a method of synthesizing a CO_2-philic analog of a CO_2-phobic compound, comprising the step of: reacting the CO_2-phobic compound with a CO_2-philic compound to create the CO_2-philic analog. Preferably, the CO_2-philic compound contains no F or Si.

Preferably, the CO_2-philic compound is a polyether substituted with at least one side group including a group that interacts favorably with or has an affinity for CO_2 (preferably a Lewis base group), a poly(ether-carbonate), a poly(ether-carbonate) substituted with at least one side group including preferably a Lewis base, a vinyl polymer substituted with at least one side group including preferably a Lewis base, a poly(ether-ester) or a

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poly(ether-ester) substituted with at least one side group including preferably a Lewis base. Preferably, the CO_2-philic compound contains no F or Si atoms. The CO_2-philic analog of the CO_2-phobic compound has increased

5   solubility or miscibility in CO_2 (that is, increased CO_2-philic nature) compared to the CO_2-phobic compound.

In one embodiment, the CO_2-philic compound is a polyether copolymer including the repeat units
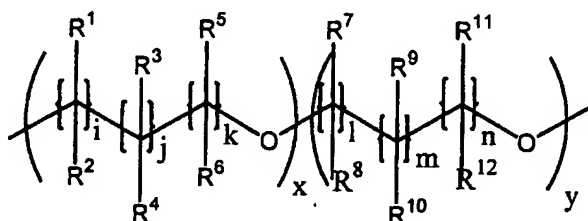
10   wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, and R^{12} are, independently, the same or different, H, an alkyl group, $-(R^{22'})_z R^{22}$, or R^4 and R^6 form of carbon cyclic chain of 3 to 8 carbon atoms. $R^{22'}$ is a spacer or connecting group, and preferably is an alkylene group, and z is 0 or 1.

15   R^{22} is a group that interacts favorably with CO_2 and is preferably a Lewis base group. Preferably, at least one of R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, and R^{12} is $-(R^{22'})_z R^{22}$.

In the above equation, i, j, k, l, m, and n are

20   independently, the same or different, 0, 1 or 2. At least one of i, j, and k is 1 or 2, and at least one of l, m, and is 1 or 2. x and y are integers. Preferably, i, j, k, l, m, and n are 0 or 1. More preferably, i is 0, j is 1, k is 1, l is 0, m is 1 and n is 1. In the case that one of i, j,

k, l, m, or n is 2, each of the substituents on the two carbon atoms can be different. In that regard, for example, $-(CR^1R^2)_2-$ expands to $-(CR^1R^2-CR^{1'}R^{2'})-$ wherein R^1, R^2, $R^{1'}$, and $R^{2'}$ are, independently, the same or different, H, an alkyl group, $-(R^{22'})_zR^{22}$. Likewise, pendant R's on adjacent carbons can form a carbon chain of 3 to 8 carbon atoms.

In several embodiments $R^{22'}$ is $-(CH_2)_a-$ and a is an integer between 0 and 5. Preferably, a is 1 or 2. Suitable Lewis base groups R^{22}, include, but are not limited to, carbonyl-containing groups such as $-O-C(O)-R^{23}$ or $-C(O)-R^{23}$, $-O-P(O)-(O-R^{23})_2$, or $-NR^{23}R^{23'}$, wherein R^{23} and $R^{23'}$ are preferably independently, the same or different, an alkyl group.

In one embodiment in which i is 0, j is 1, k is 1, l is 0, m is 1 and n is 1, R^3, R^4, R^5, R^9, R^{10}, and R^{11} are H, R^6 is an alkyl group and R^{12} is a Lewis base. For example, the lewis base group can be $O-C(O)-R^{23}$. In one such embodiment, R^{23} is a methyl group. In one embodiment the methyl group is substituted with a Cl ($-CH_2Cl$).

Preferably, the polyether copolymer contains no F or Si atoms.

In the repeat units of the polyether, x and y are integers. Preferably x and y are each at least 1. Preferably, the total chain length of the CO_2-philic group (x + y) is less than approximately 400 repeat units. More preferably, the total chain length of the CO_2-philic group (x + y) is less than approximately 200 repeat units. For many application (for example, surfactants) the total chain

length is preferably between 5 and 50 repeat units. More preferably, the chain length in such applications is between approximately 20 to 40 repeat units. The percentage of repeat units including a Lewis base group is preferably in the range of approximately 1 to approximately 50 %. More preferably, the percentage of repeat units including a Lewis base group is in the range of approximately 5 to approximately 35 %. Even more preferably, the percentage of repeat units including a Lewis base group is in the range of approximately 10 to approximately 25 %.

In another embodiment, the CO_2-philic compound is a poly(ether-carbonate) copolymer including the repeat units:
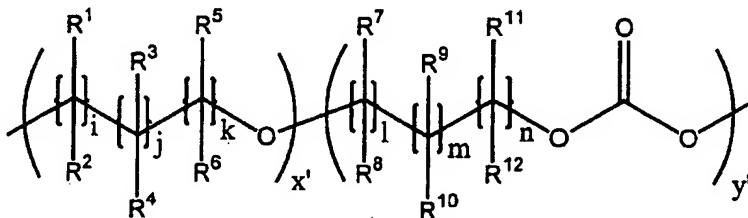

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, and R^{12} are, independently, the same or different, H, an alkyl group, $-(R^{22'})_z R^{22}$, or R^4 and R^6 form of carbon cyclic chain of 3 to 8 carbon atoms as described above. Likewise, i, j, k, l, m and n are as described above (0, 1 or 2). Preferably, i, j, k, l, m and n are 0 or 1. In several embodiments, i and l are 0, and j, k, m and n are 1. In this copolymer a Lewis base group is incorporated into the copolymer backbone. The copolymer can also include one or more pendant groups that react favorably with CO_2 (preferably, Lewis base groups). Preferably, the poly(ether-carbonate) copolymer contains no F or Si atoms.

In one embodiment i and l are 0, j, k, m and n are 1, R^3, R^4, R^5, R^9, R^{10}, and R^{11} are H, R^6 is an alkyl group (for example, a methyl group) and R^{12} is an alkyl group (for example, a methyl group).

In the repeat units of the polycarbonate, x' and y' are integers and, preferably, each is at least 1. Preferably, the total chain length of the CO_2-philic group (x' + y') is less than approximately 400 repeat units. More preferably, the total chain length of the CO_2-philic group is less than approximately 200 repeat units. For many application (for example, surfactants) the total chain length is preferably between 5 and 50 repeat units. More preferably, the chain length in such applications is between approximately 20 to 40 repeat units. The percentage of repeat units including the carbonate linkage (that is, the Lewis base in the copolymer backbone indicated by y') is preferably in the range of approximately 1 to approximately 50 %. More preferably, the percentage of repeat units including the carbonate linkage is in the range of approximately 5 to approximately 35 %. Even more preferably, the percentage of repeat units including the carbonate linkage is in the range of approximately 10 to approximately 25 %.

In one aspect, the vinyl polymer is a copolymer including the repeat units:
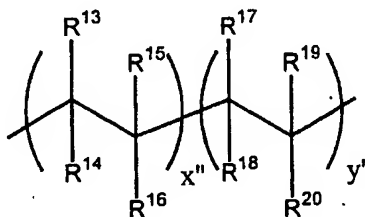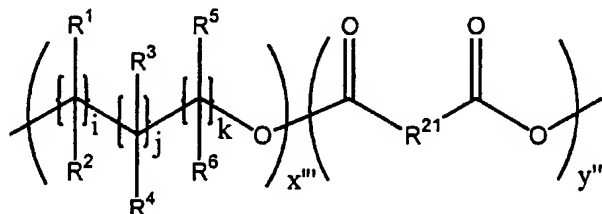
wherein R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, and R^{20} are, independently, the same or different, H, an alkyl group, an alkenyl group, $-O-R^{24}$, $-(R^{22'})_z R^{22}$, wherein, z, $R^{22'}$ and R^{22} are as described above. Preferably, at least one of R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, and R^{20} is $-(R^{22'})_z R^{22}$. x" and y" are integers. The vinyl copolymer preferably contains no F or Si atoms.

In several embodiment, $R^{22'}$ is $-(CH_2)_a-$ and a is an integer between 0 and 5. In such embodiments, a is preferably 1 or 2 and R^{22} is, for example, $-O-C(O)-R^{23}$, $-C(O)-R^{23}$, $-O-P(O)-(O-R^{23})_2$, or $-NR^{23}R^{23'}$, wherein R^{23} and $R^{23'}$ are independently, the same or different, an alkyl group.

In the polyvinyl copolymer, x" and y" are integers and preferably each is at least 1. Preferably, the total chain length of the CO_2-philic group (x" + y") is less than approximately 400 repeat units. More preferably, the total chain length of the CO_2-philic group is less than approximately 200 repeat units. For many application (for example, surfactants) the total chain length is preferably between 5 and 50 repeat units. More preferably, the chain length in such applications is between approximately 20 to 40 repeat units. The percentage of repeat units including a Lewis base is preferably in the range of approximately 1 to approximately 50 %. More preferably, the percentage of repeat units including a Lewis base is in the range of approximately 5 to approximately 35 %. Even more preferably, the percentage of repeat units including a Lewis base is in the range of approximately 10 to approximately 25 %.

In another aspect, the CO_2-philic compound is a poly(ether-ester) copolymer including the repeat units

$$\left(\left(\begin{array}{c}R^1\\|\\C\\|\\R^2\end{array}\right)_i\left(\begin{array}{c}R^3\\|\\C\\|\\R^4\end{array}\right)_j\left(\begin{array}{c}R^5\\|\\C\\|\\R^6\end{array}\right)_k O\right)_{x'''}\left(\begin{array}{c}O\\\|\\C\end{array} R^{21} \begin{array}{c}O\\\|\\C\end{array} O\right)_{y'''}$$

wherein R^1, R^2, R^3, R^4, R^5 and R^6 are as defined above, and i, j and k are as defined above (0, 1 or 2). Preferably, i, j, k, l, m and n are 0 or 1. In several embodiments, i and l are 0, and j, k, m and n are 1. R^{21} is a connecting group that can, for example, be an alkylene group (a difunctional alkyl group), a cycloalkylene group (a difunctional cycloalkyl group), a difunctional ester group, (for example, $-(CR^{25}R^{26})_{p'}-C(O)-O-(CR^{27}R^{28})_{p''}-$), a difunctional ether group (for example, $-(CR^{25}R^{26})_{p'}-O-(CR^{27}R^{28})_{p'}$. R^{25}, R^{26}, R^{27} and R^{28} are preferably independently H or an alkyl group. x''' and y''' are integers.

Such poly(ether ester) copolymers include a Lewis base group in the copolymer backbone. The copolymer can also include one or more pendant groups that interact favorably with CO_2 (preferably, Lewis base groups). In that reagard, at least one of R^1, R^2, R^3, R^4, R^5 and R^6 can be $-(R^{22'})_z R^{22}$, wherein $R^{22'}$ and R^{22} are as defined above. The group R^{22} can, for example, be $O-C(O)-R^{23}$, $-C(O)-R^{23}$, $-O-P(O)-(O-R^{23})_2$, or $-NR^{23}R^{23'}$, wherein R^{23} and $R^{23'}$ are as defined above.

In a number of embodiments, $R^{22'}$ is $-(CH_2)_a-$ and a
is an integer between 0 and 5. In several such embodiments,
a is 1 or 2 and i is 0, j is 1, and k is 1.

In the polyvinyl copolymer, x''' and y''' are
integers and preferably each is at least 1. Preferably, the
total chain length of the CO_2-philic group $(x''' + y''')$ is
less than approximately 400 repeat units. More preferably,
the total chain length of the CO_2-philic group is less than
approximately 200 repeat units. For many application (for
example, surfactants) the total chain length is preferably
between 5 and 50 repeat units. More preferably, the chain
length in such applications is between approximately 20 to
40 repeat units. The percentage of repeat units including
the ester linkage (that is, the Lewis base in the copolymer
backbone indicated by y''') is preferably in the range of
approximately 1 to approximately 50 %. More preferably, the
percentage of repeat units including the carbonate linkage
is in the range of approximately 5 to approximately 35 %.
Even more preferably, the percentage of repeat units
including the carbonate linkage is in the range of
approximately 10 to approximately 25 %.

The polyether copolymers, poly(ether-carbonate)
copolymers, vinyl copolymers and poly(ether-ester
copolymers) described above are preferably not alternating
copolymers. Moreover, other monomer or repeat units can
incorporated in the copolymers (for example, between the
repeat units set forth above).

The present invention also provides a surfactant
for use in carbon dioxide, the surfactant includes a
CO_2-phobic group covalently linked to a CO_2-philic segment,

wherein the CO_2-philic segment includes a polyether substituted with at least one side group including a group that interacts favorably with CO_2 (preferably a Lewis base group), a poly(ether-carbonate), a poly(ether-carbonate) substituted with at least one side group including preferably a Lewis base, a vinyl polymer substituted with at least one side group including preferably a Lewis base, a poly(ether-ester) or a poly(ether-ester) substituted with at least one side group including preferably a Lewis base. The polyether, polycarbonate, vinyl polymer and poly(ether-ester) are preferably copolymers as described above.

The CO_2-phobic group of the surfactants of the present invention can be generally any head group usable in surfactants, including, but not limited to, H, a carboxylic acid group, a hydroxy group, a phosphato group, a phosphato ester group, a sulfonyl group, a sulfonate group, a sulfate group, a branched or straight chained polyalkylene oxide group, an amine oxide group, an alkenyl group, a nitryl group, a glyceryl group, an aryl group unsubstituted or substituted with an alkyl group or an alkenyl group, a carbohydrate unsubstituted or substituted with an alkyl group or an alkenyl group, an alkyl ammonium group, or an ammonium group. Carbohydrates groups include, for example sugars such as sorbitol, sucrose, or glucose. The CO_2-phobic group may likewise include an ion selected from the group of H^+, Na^{+2}, Li^+, K^+, NH_4^+, Ca^{+2}, Mg^{+2}, Cl^-, Br^-, I^-, mesylate and tosylate.

The present invention also provides a chelating agent for use in carbon dioxide. The chelating agent includes a CO_2-phobic chelating group covalently linked to a CO_2-philic segment, wherein the CO_2-philic segment includes

a polyether substituted with at least one side group including a group that interacts favorably with CO_2 (preferably a Lewis base), a polycarbonate, a polycarbonate substituted with at least one side group including preferably a Lewis base, a vinyl polymer substituted with at least one side group including preferably a Lewis base a poly(ether-ester) or a poly(ether-ester) substituted with at least one side group including preferably a Lewis base. The polyether, polycarbonate, vinyl polymer and poly(ether-ester) are preferably copolymers as described above. The chelating group may, for example, be a polyaminocarboxillic acid group, a thoicarbamate group, a dithoicarbamate group, a thiol group, a dithiol group, a picolyl amine group, a bis(picolyl amine) group or a phosphate group.

The present invention also provides a method of synthesizing a CO_2-phile including the step of copolymerizing at least two monomers, wherein a polymer formed from homopolymerization of one of the monomers has a

5   T_g of less than approximately 250 K and a steric factor less than approximately 1.8. At least one of the monomers results in a group in the copolymer that interacts favorably with CO_2 (for example, a Lewis base group), and the resultant CO_2-phile does not contain both hydrogen bond

10   donors and acceptors. For example, a first monomer can be selected wherein a polymer formed from homopolymerization of the first monomers has a T_g of less than approximately 250 K and a steric factor less than approximately 1.8, while a second monomer results in a repeat unit within the copolymer

15   that includes a Lewis base group (either in the copolymer backbone or pendant therefrom).

The CO_2-phile is preferably a polyether, a polycarbonate, a vinyl copolymer or a poly(ether-ester) as described above. A Lewis base group, when pendant, is preferably separated from the CO_2-phile backbone by 0 to 5 atoms (more preferably, 1 to 2 atoms).

The present invention also provides a method of synthesizing a CO_2-phile comprising the step of copolymerizing carbon dioxide and at least one oxirane. The oxirane may, for example, be epichlorohydrin, ethylene oxide, propylene oxide or cyclohexene oxide.

Prior to the present invention, only fluorous and silicon polymers were thought to be generally suitable for use in creating CO_2-philic analogs of CO_2-phobic compounds. However, the hydrocarbon CO_2-philic compounds and groups of the present invention exhibit phase boundaries in CO_2 that occur at pressures comparable to those of fluorinated polyethers of similar chain length, and substantially lower than those of silicones. Moreover, these hydrocarbon CO_2-philic groups are substantially less expensive to manufacture and use than fluorinated or silicon compounds.

The CO_2-philic compounds and groups of the present invention can be used in a wide variety of applications including, for example, the cleaning industry in which they can be incorporated into surfactants, detergents, fabric softeners and antistatic agents. As chelating agents, they can be used, for example, in metal recovery. The CO_2-philic compounds and groups of the present invention can also be incorporated in cleaners used in the electronics industry to, for example, remove oils, greases and other residues from electronic components. The CO_2-philic compounds can

further be used in dispersants for polymers or inorganic particles (stabilizers), affinity ligands for proteins, catalyst ligands and coatings.

Brief Description of the Drawings

5   Figure 1 illustrates a block diagram of an embodiment of CO_2-philic material design of the present invention.

        Figure 2 illustrates a method of synthesizing poly(epichlorohydrin-glycidyl acetate).

10   Figure 2 illustrates the phase behavior of the acetate functionalized poly(epichlorohydrin).

        Figure 3 illustrates phase behavior of acetate functionalized epichlorohydrin N = 25 repeat units (1 - 33% acetate; 2 - 40 % acetate; 3 - PO homopolymer (also 25
15   repeat units); 4 - 45 % acetate).

        Figure 4 illustrates phase behavior of acetate functionalized poly(epichlorohydrin) (1 - Epichlorohydrin homopolymer; 2 - 28 % acetate; 3 - 100 % acetate; 4 - 33 % acetate; 5 38 % acetate).

20   Figure 5 illustrates phase behavior of functionalized poly(epichlorohydrin) with 33% acetate (1- N=25 repeat units; 2- N=7 repeat units).

Figure 6 illustrates several embodiment of sterically hindered aluminum catalysts.

Figure 7 illustrates synthesis of polycarbonate copolymers from an oxirane such as propylene oxide and
5   carbon dioxide.

Figure 8 illustrates the phase behavior propylene oxide-carbon dioxide (PO/CO_2) polycarbonate copolymers with N= 25 repeat units (1- PO/CO_2 copolymer with 56 % carbonate; 2- PO homomopolymer; 3- PO/CO_2 copolymer with 40 %
10   carbonate).

Figure 9 illustrates the phase behavior propylene oxide-carbon dioxide polycarbonate copolymers compared to the phase behavior of a fluororether (1- PO/CO_2 copolymer with N= 220 repeat units and 15 % carbonate; 2- Krytox
15   (available from Dupont) with N= 176 repeat units).

Figure 10 illustrates the phase behavior or an ethylene oxide-carbon dioxide (EO/CO_2) polycarbonate copolymer compared to polyethylene oxide homopolymer (PEO) (1- EO/CO_2 copolymer with N= 103 repeat units and 33.7 %
20   carbonate; 2- PEO with N= 16).

Figure 11 illustrates the phase behavior cyclohexene oxide-carbon dioxide (CHO/CO_2) polycarbonate copolymers (1- 47 % carbonate with N= 27; 2- 40 % carbonate with N= 20; 3- 50 % carbonate with N=16).

25   Figure 12 illustrates phase behavior cyclohexene oxide-carbon dioxide polycarbonate copolymers with low

content of carbonate units (1- 8.8 % carbonate with N= 124;
2- 2.3 % carbonate with N=88).

   Figure 13   illustrates   phase   behavior   of
poly(propylene glycol) diol (1), poly(propylene glycol)
5   monobutyl ether (2) and poly(propylene glycol) acteate (3)
with 21 repeat units.

   Figure 14   illustrates   phase   behavior   of
epichlorohydrin/CO_2 copolymer compared to acetate modified
poly(epichlorohydrin) (1- ECH/CO_2 copolymer with N= 17 and
10   25 % carbonate; 2- Modified poly(epichlorohydrin) (PECH)
with N= 25 and 45 % acetate).

   Figure 15 illustrates phase behavior of vinyl
acetate and ethyl vinyl ether homopolymers (1- poly(vinyl
acetate) with 90 repeat units; 2- Poly(ethyl vinyl ether)
15   with 20 repeat units; 3- poly(vinyl acetate) with 70 repeat
units).

   Figure 16 illustrates phase behavior of vinyl
acetate/ethyl vinyl ether copolymers and vinyl acteate
homopolymer with 90 repeat units (1- 39.8 % vinyl acetate
20   (VA); 2- 22.4 % VA; 3- VA homopolymer).

   Figure 17 illustrates phase behavior of vinyl
acetate/ethyl vinyl ether copolymers and vinyl acetate
homopolymer with 70 repeat units (1- 67 % VA; 2- 63 % VA; 4-
VA homopolymer; 4- 18.47 % VA.)

Figure 18 illustrates phase behavior of vinyl acetate/ethyl vinyl ether copolymers (1- 135 repeat units and 46.6 % VA; 2- 90 repeat units and 39.8 % VA).

5   Figure 19 illustrates the general design of an analog of a CO_2-phobic compound that is made miscible or soluble in CO_2 by incorporation of one or more CO_2-philic groups.

Detailed Description of the Invention

As used herein, the term "polymer" refers to a
10   compound having multiple repeat units (or monomer units) and includes the term "oligomer," which is a polymer that has only a few repeat units. The term "copolymer" refers to a polymer including two or more dissimilar repeat units (including terpolymers - comprising three dissimilar repeat
15   units - etc.).

The terms "alkyl", "alkenyl", "aryl", "akylene" and other groups refer generally to both unsubstituted and substituted groups (that is, having one or more hydrogen atoms replaced with one or more substituent groups) unless
20   specified to the contrary. Unless otherwise specified, alkyl groups are hydrocarbon groups and are preferably C_1-C_{10} (that is, having 1 to 10 carbon atoms) alkyl groups, and more preferably C_1-C_6 alkyl groups, and can be branched or unbranched, acyclic or cyclic. Unless otherwise
25   specified, the term "aryl group" refers generally to a phenyl group or to a napthyl group. The term "alkylene group" refers generally to bivalent forms of alkyl groups

and can be linear (for example, $-(CH_2)_a-$), branched, acyclic or cyclic (for example, a bivalent form of cyclohexane). Alkylene groups are preferably C_1-C_{10} alkylene groups and, more preferably, C_1-C_5 alkylene groups.

5   The term "alkenyl" refers to a straight or branched chain hydrocarbon groups with at least one double bond, preferably with 2-10 carbon atoms, and more preferably with 2-6 carbon atoms (for example, $-CH=CHR^4$ or $-CH_2CH=CHR^4$, wherein R^4 is an alkyl group).

10   Preferably, the groups of the present invention, if substituted, are substituted with substituent groups that enhance or at least do not substantially negatively effect the CO-philic nature of the CO-philic compound or group. In addition to Lewis base groups, such substituents, include,
15 but are not limited to alkyl groups, alkoxy groups, ether groups, Cl, and alkenyl groups.

          As used herein and understood in the art, the term "CO_2-philic" preferably refers generally to compounds and groups that are appreciably soluble in or miscible in carbon
20 dioxide, preferably at pressures below approximately 300 atm. More preferably, the compounds and groups are appreciably soluble in or miscible in carbon dioxide at pressures below approximately 200 atm. Most preferably, the compounds and groups are appreciable soluble in or miscible
25 in carbon dioxide at pressures below approximately 125 atm. Likewise, such solubility or miscibility is preferably exhibited at temperatures in the range of approximately 0 to 100°C (more preferably, in the range of approximately 0 and 50°C; most preferably, between approximately 0 and 30°C).

As used herein, the term "CO_2-phobic" refers generally to compounds and groups that exhibit little solubility or miscibility in carbon dioxide over the pressure and temperature ranges set forth above.

5   It is difficult to quantify a cutoff point as to whether a particular type of compound is CO_2-philic or CO_2-phobic as, for example, solubility or miscibility of a particular molecule in CO_2 depends (inversely) upon the chain length. In general, under the conditions set forth

10   above, a CO_2-philic compound of approximately 25 repeat units preferably has a solubility of at least approximately 2% by weight. More preferably, the compound has a solubility of at least approximately 2% by weight at approximately 100 repeat units. Even more preferably, the

15   compound has a solubility of at least approximately 2% by weight at greater than 200 repeat units.

Design Criteria for Hydrocarbon CO_2-philes

            In designing a hydrocarbon CO_2-phile, the free energy of mixing between the target compound and CO_2 must be

20   favorable (that is, negative) at moderate pressures for the material to be considered CO_2-philic. Although the entropy and enthalpy of mixing are coupled, one can at first treat the two factors separately by considering only the configurational entropy of mixing (entropic contributions

25   owing to segment-segment interactions can be considered later).

Heuristics to Maximize the Entropy of Mixing

One can choose structures that enhance the entropy of mixing of the CO_2-philes of the present invention and CO_2 by choosing moieties that permit relatively unfettered rotation, and thus relatively larger number of potential configurations. Although the exact mathematical description of ΔS_{mix} is still a matter for discussion, previous research on the subject suggests that the entropy of mixing of a chain molecule with a solvent will increase as the flexibility (and hence the number of configurations available) of the chain molecule increases. Decreasing molecular weight is one way to increase the number of available configurations (as a result of effects arising from segment connectivity), but it is also possible to choose molecular structures that exhibit greater inherent chain flexibility. Choosing such structures in the design of the CO_2-philes of the present invention will enhance the entropy of mixing, and hence the potential for forming a single-phase mixture with CO_2.

A useful gauge of chain flexibility is the steric factor (σ), as defined in Young, R.J., Introduction to Polymers (1981), Chapman and Hall, Ltd, London, Chapter 3:

$$<r^2>_0 = \sigma n l^2 \{(1-\cos\theta)/(1+\cos\theta)\} \qquad (1)$$

where $<r^2>_0$ is the mean squared end-to-end distance of the unperturbed chain, n is the number of segments, l is the segment length, and θ is the C-C bond angle in the main chain. The steric factor provides the ratio of the actual size of a polymer coil to that which would be measured in

the absence of hindrances to free rotation, and is thus a measure of the relative flexibility of a given polymer type. Lower values of the steric factor σ suggest higher degrees of flexibility and thus potentially higher entropy of mixing

5   with any solvent. Values of σ are tabulated for a number of polymers in Polymer Handbook 3d ed., Brandrup and Immergut, Eds. (1975) Wiley, New York.

       To optimize the configurational entropy of mixing (at constant chain length) one preferably chooses to

10   incorporate those chemical structures or repeat units that provide for high free volume and high chain flexibility. Increasing specific free volume and chain flexibility decreases the glass transition temperatures (T_g). Therefore, low T_g and low steric factor can be used as

15   "markers" to help guide the choice of chemical structure of the CO_2-philes of the present invention.

       Chain topology (branched vs. linear) can also affect the entropy of mixing in that higher degrees of branching increase the entropy of mixing versus linear

20   analogs of the same number of repeat units. See Kleintjens, L.A.; Koningsveld, R.; Gordon, M.; Macromolecules (1980), 13, 303.

       Therefore, to promote high entropy of mixing in the CO_2-philes of the present invention, materials with high

25   chain flexibility and free volume (and thus relative low T_g and relatively low σ as discussed above) that include branched structures are preferably synthesized.

Effect of CO_2-Phile Structure on the Enthalpy of Mixing

It is also desirable to choose structures for inclusion into the CO_2-philes of the present invention that will enhance solute-solvent interactions while not
5 increasing the strength of solute-solute (or solvent-solvent) interactions to the point where dissolution in CO_2 is prevented.

Materials with relatively weak self-interaction will tend to exhibit low cohesive energy density, and hence
10 low values of both the interfacial tension and solubility parameter. Favorable cross interactions can also play a significant role in determining the phase behavior of polymers in CO_2. Specific interactions in CO_2-solute systems can, for example, be of the dipole-quadropole
15 variety, or also Lewis acid/Lewis base, given that CO_2 is a known Lewis acid. The importance of favorable cross-interactions decreases as the temperature is raised.

In light of the above, to optimize the enthalpy of mixing, one preferably begins with a base material having a
20 low cohesive energy density to minimize the impact of solute-solute interactions (this base material should also exhibit a low T_g and steric factor, as indicated in the previous section). However, functional groups that interact favorably with CO_2 (preferably, Lewis bases) are preferably
25 added to enhance cross interactions.

Given the criteria developed above through entropic and enthalpic considerations, the CO_2-philic

hydrocarbons of the present invention are preferably synthesized as a copolymer wherein:

1.   At least one of the monomers/repeat units preferably provides high flexibility and high free volume, as evidenced by low T_g and low steric parameter, to enhance the entropy of mixing, and also a low cohesive energy density, to minimize the impact of solute-solute interactions. In that regard, a polymer formed from polymerization of such a monomer preferably has a T_g of less than approximately 250 K. More preferably, the T_g is less than approximately 200 K. The steric factor of a polymer formed from polymerization of such a monomer is preferably less than approximately 1.8. More preferably, the steric factor is less than approximately 1.5. Most preferably, the steric factor is less than approximately 1.3.

2.   At least one of the monomers/repeat units preferably contains a group or groups that are known to interact specifically with CO_2 (for example, Lewis bases), yet the resultant CO_2-phile preferably does not contain both hydrogen bond donors and acceptors. The presence of both hydrogen bond donors and acceptors will tend to lower flexibility, and inflate both T_g and the cohesive energy density.

3.   The functional groups described in (2) above are preferably separated from the polymer backbone by 1 or 2 atom spacer when present in a side chain.

Use of a flexible chain (1) with a branched architecture (3) ensures that the entropy of mixing will be as high as possible. Further, choosing a base material with a low cohesive energy density reduces the strength of

5   solute-solute interactions, and thus favors mixing. Finally, inclusion of functional groups (preferably, Lewis bases) that interact favorably (albeit weakly) with CO_2 produce favorable solute-CO_2 interactions, and thus enhance the enthalpy of mixing. However, adding such groups will

10   likely also raise the cohesive energy density, and thus the optimal number of such groups is such that the two effects are preferably balanced.

A copolymer including two monomers exhibiting the above criteria is represented graphically in Figure 1.

15   (A)   In Figure 1, Monomer 1 (M_1), contributes to high flexibility, high free volume, and weak solute/solute interactions (low cohesive energy density or interfacial tension). As described above, low Tg and steric parameter are generally used as evidence for high

20   flexibility and free volume in polymeric materials. These factors combine to create a favorable entropy of mixing for the copolymer in CO_2, as well as weak solute-solute interactions, easing dissolution into CO_2.

(B)   Monomer 2 (M_2), produces specific solute/solvent

25   interactions between the polymer and CO_2, through a group with affinity for carbon dioxide such as a Lewis base group (for example, a carbonyl group) in a side chain or in the backbone of the polymer.

Ideally, interactions between M_1 and M_2 should be enthalpically unfavorable, further helping to promote dissolution in carbon dioxide. It is possible that this feature is a strong contributor to the low miscibility

5   pressures of fluoroacrylate polymers in CO_2, in that interactions between the fluorinated side chains and acrylate backbone of this material are likely to be unfavorable. Because use of a homopolymer of either M_1 or M_2 only serves to optimize part of the free energy, if both

10 monomer 1 and monomer 2 are chosen in the proper proportions the copolymer will be more soluble than either of the homopolymers.

In addition to the location of the phase boundaries in P-x space, the effect of temperature on

15 miscibility pressure is also of importance. If increasing temperature raises the miscibility pressure (LCST type behavior) for a particular CO_2-phile, increasing chain flexibility (through alterations to copolymer composition) may favorably impact phase behavior. On the other hand, if

20 UCST behavior is observed (decreasing miscibility pressure as temperature increases), then increasing the concentration of functional groups that interact with CO_2 is recommended.

The present inventors have discovered that adherence to the criteria set forth above in designing

25 CO_2-philes, enables synthesis of CO_2-philes that are strongly CO_2-philic without the necessity of incorporating fluorine or silicon atoms. Monomers that produce polymers (and that preferably do not contain fluorine or silicon) with low cohesive energy density and low T_g include, for

30 example, alpha olefins (for example, ethylene and/or propylene), dienes (for example, butadiene and/or isoprene),

and various cyclic ethers. Functional groups that are likely to interact favorably with CO_2 include Lewis bases such as carbonyls, tertiary amines, and phosphonyls.

Some of the above-identified monomeric base materials (for example, polyethylene and polybutadiene) can readily crystallize in certain forms in which chain packing is straightforward. Crystallization is not desirable in the CO_2-philes of the present invention because the operating temperature (and thus the pressure) required to form a single phase solution in CO_2 will be elevated (to melt the material), increasing the cost of a potential processes. Fortunately, incorporation of a comonomer (preferably in an atactic fashion) reduces order in the molecule and thereby reduces the potential to pack and crystallize.

The entropy of mixing drops as the chain length of the solute increases. Preferably, the total chain length of the CO_2-philic group is less than approximately 400 repeat units. More preferably, the total chain length of the CO_2-philic group is less than approximately 200 repeat units. For many application (for example, surfactants) the total chain length is preferably between 5 and 50 repeat units. More preferably, the chain length in such applications is between approximately 20 to 40 repeat units.

Although the entropy and enthalpy of mixing have been treated separately in the present analysis, it is clear that they are inextricably linked. As the number specific interactions (CO_2-solute) increases, the enthalpy of mixing may become more favorable but the entropy of mixing will decrease. Increasing the number of comonomers with Lewis base groups in the chain (either in the backbone or pendant)

can hinder rotation about the chain, also reducing the entropy of mixing. Likewise, substitutions or side groups other than Lewis base groups on the comonomers can also hinder rotation.

5   Finally, as mentioned above, increasing the number of Lewis base functional groups will also raise the cohesive energy density, and thus a point may be reached where further incorporation of such groups is an enthalpic detrement, rather than an advantage. In the CO_2-philes of
10   the present invention, the preferred number of functionalized comonomers (much like a "bound" co-solvent) per chain is that which provides a suitable balance between enthalpy gain through favorable cross-interactions, enthalpy loss from increased solute cohesive energy density, and
15   entropy loss and is readily determined experimentally.

MODEL STUDIES WITH CARBONYL-FUNCTIONAL POLY(DIMETHYL SILOXANE)

        The effect of side chain functionalization with Lewis bases on the CO_2 phase behavior of a model silicone CO_2-phile was studied. Silicones are considered CO_2-philic,
20   although not as strongly CO_2-philic as fluorinated ethers and fluorintated acrylates. It was observed that silicones exhibit UCST type behavior (as temperature increases, the pressure required to solubilize a given amount of material drops), which suggested that the enthalpy of mixing of these
25   materials with CO_2 might be improved through the incorporation of Lewis bases in side chains. Silicones exhibit amongst the lowest T_g (150K) and steric parameter (1.39) observed in synthetic polymers, and hence it would appear that chain flexibility (and thus the entropy of
30   mixing) is not an area requiring extensive improvement.

Functionalized silicones were prepared via the hydrosilation of model dimethyl siloxane-hydromethyl siloxane oligomers (25 repeat units total, with 1, 2, or 5 hydromethyl groups per chain, received from Gelest, Inc.)

5   over a platinum catalyst. Allyl acetate or 1 hexene were used to generate the side chains, to allow comparison of the efficacy of adding Lewis base groups to adding simply methylene units. The carbonyl group was thus separated from the main chain by a propyl spacer.

10   The phase behavior of the model CO_2-philes was measured as described previously in Hoefling, T.A.; Newman, D.A.; Enick, R.M.; Beckman, E.J.; J. Supercrit. Fl. (1993), 6, 165, using a variable volume high-pressure view cell. Phase behavior results were quite dramatic, in that addition

15   of five acetate functional side chains to the silicone oligomer lowered the cloud point curve by over 2500 psi at room temperature. Addition of simple alkyl side chains raised the cloud point curves to higher pressures. Finally, the magnitude of the change in the location of the cloud

20   point curve was found to be proportional to the number of side chains.

This model study confirmed that addition of Lewis base groups in side chains removed from the polymer backbone of a known silicon-containing CO_2-philic compound renders

25   the material "more CO_2-philic." Subsequently, studies were performed upon hydrocarbons that did not contain F or Si to determine whether addition of Lewis base groups would improve or establish CO_2-philic nature in such compounds.

FUNCTIONALIZED POLYETHER COPOLYMERS

Polyethers are known to exhibit low T_g's (typically, in the range of approximately 190 to approximately 230 K) and relatively low cohesive energy densities. Previous studies have shown that polyethers are more "CO_2-philic" than many other common polymers, yet significantly less so than fluorinated polymers or silicones. The present studies explored the effect of side chain functionalization with Lewis bases (for example, a functional group comprising a carbonyl group) on the phase behavior of model polyethers in CO_2. Carbonyls have been shown to interact favorably with carbon dioxide. The effect of C=O placement in polyethers, as well as the effect of the extent of functionalization with carbonyl groups were studied. The phase behavior of a homopolymer of propylene oxide (PO) with the same number of repeat units was used as a baseline for comparison.

Lewis base functionalized PO (and/or, for example ethylene oxide (EO)) copolymers may, for example, be generated via copolymerization of either of the two oxiranes with the acetate-functional analog synthesized from glycidol and acryloyl chloride. It has also been shown previously that tertiary amines interact favorably with CO_2 via an acid-base mechanism. Reaction between an epichlorohydrin homo- or copolymer and a dialkyl amine will produce a tertiary amine-functional polyether. One can, for example, synthesize a compound with pendant phosphonyl groups via reaction of glycidol with chloro (diethyl) phosphonate, followed by copolymerization of the new monomer with, for example, propylene oxide.

In one study, epichlorohydrin was polymerized using boron trifluoride etherate at temperatures below 0°C, and characterized via GPC. Acetate-functional derivatives (see Figure 2) were then prepared via reaction of potassium

5   acetate with the epichlorohydrin polymer in the presence of a phase transfer catalyst. Phase behavior presented in Figure 3 shows that addition of acetate groups lowers the cloud point pressures considerably.

The Effect of Side Chain Functionalization on Solubility

10   A homopolymer of epichlorohydrin (25 repeat units) exhibits cloud point pressures above the limits of the instrument used (400 atmospheres, or 6000 psi) for concentrations greater than 0.5 weight %. As one can see from Figure 3, although the homopolymer of epichlorohydrin

15   is insoluble at the operating conditions, the acetate modified polymers are soluble in CO_2, and their cloud point pressures decrease as the amount of acetate is increased. Thus, a polymer modified with 45 % acetate exhibits lower cloud point pressures than a homopolymer of propylene oxide

20   of the same chain length.

        A lower molecular weight (seven repeat units) poly(epichlorohydrin) was also modified with different amounts of acetate groups, and their solubilities compared (Figure 4). The cloud points dropped by 100 atm as the

25   percent acetate incorporated into the polymer increased from 28 to 38 %, yet the cloud point pressures of a 100 % acetate were higher. It is believed that the acetate groups act like a bound cosolvent. However, as the amount of acetate increased a point of diminishing returns was reached.

Although increasing the amount of acetate enhances CO_2-polymer interactions, it also stiffens the chain and likely enhances polymer-polymer interactions as well. Comparing poly(epichlorohydrin) with 7 and 25 repeat units (Figure 5)

5   with the same amount of acetate (33 %), it was seen that the cloud points of the two differed by as much as 70 atm, as expected.

POLYETHER/POLYCARBONATES COPOLYMERS

It was believed that incorporation of the Lewis

10 bases such as carbonyl groups into side chains would be the most productive route to increase miscibility or solubility in CO_2, as a result of enhancement of both the enthalpy and entropy of mixing. Nevertheless, the incorporation of carbonyls into the polymer backbone via copolymerization of

15 CO_2 itself with propylene oxide (PO), cyclohexene oxide (CHO) and ethylene oxide (EO). Sterically hindered alkoxy aluminum catalysts (examples of which are illustrated in Figure 6) were identified that copolymerize propylene oxide and other cyclic ethers with CO_2 at much higher efficiencies

20 (greater than 200 grams of polymer per gram of aluminum) than has previously been reported. These catalysts are living in character (yields in the range of 200 - 1200 g polymer/g catalyst) with one type of site available for polymerization, and can be monofunctional or difunctional.

25 The extent to which CO_2 is incorporated into the polymer depends on the temperature and pressure at which the polymerization is carried out, as well as on the nature of sterically hindered substituents attached to the aluminum atoms and on the oxirane type.

Using the sterically hindered alkoxy aluminum catalysts, a series of PO/CO_2 copolymers were synthesized as illustrated in Figure 7. In a typical experiment, aluminum chloride was reacted with first, propylene glycol, then 2,6

5 di-isobutyl, 4-methyl phenol at 0°C under argon to generate the catalyst. The catalyst was characterized via ^1H and ^{27}Al NMR. Other sterically hindered aluminum catalysts were prepared similarly by changing the nature of the alcohols. Copolymerizations were conducted between CO_2 and, for

10 example, ethylene oxide (EO), propylene oxide (PO), and cyclohexene oxide (CHO) at temperatures between 5°C and 60°C (depending upon oxirane type) and pressure between 800 and 2500 psi, for times up to 24 hours. The molecular weight was controlled via the ratio of oxirane to catalyst.

15 Typically, catalyst was charged to a stainless steel 50 cc reactor under argon, followed by CO_2 at its vapor pressure. The oxirane was then charged using a manual syringe pump, and the pressure and temperature brought to their desired points. At a pre-designated time, the polymerization was

20 quenched with acidic methanol, and the residual oxirane was removed under vacuum. Furthermore, these types of copolymers can also be formed by the reaction of phosgene and diols.

Phase behavior studies in CO_2 indicated that

25 copolymerization of CO_2 and oxiranes produce CO_2-philic hydrocarbons. Only a small percentage of carbonate repeat units was needed to produce a CO_2-philic material. Further, choice of the correct percentage of carbonate repeat units lead to phase behavior that is superior to either of the

30 homopolymers.

Comparing PO/CO$_2$ copolymers with 25 repeat units (Figure 8) one can see that a copolymer with 56 % carbonate is less CO$_2$-philic than a homopolymer of PO, but a polymer with 40 % carbonate exhibits miscibility pressures lower

5 than those of the homopolymer. A polycarbonate homopolymer (that is, a completely alternating CO$_2$/propylene copolymer) with 25 repeat displays miscibility pressures beyond the limits (6000 psi) of the instrument used. These results are consistent with the design hypothesis of Figure 1, that if

10 the certain proportions of monomer 1 and monomer 2 as described in the above criteria are chosen, the copolymer will be more soluble than either of the homopolymers.

Indeed, PO/CO$_2$ copolymers are apparently more CO$_2$-philic than fluoroether polymers, in that the cloud points

15 of a 250 repeat unit PO/CO$_2$ copolymer (15.4 % carbonate) were significantly lower than those for a poly(perfluoroether) (Krytox™ available from DuPont) with 175 repeat units (Figure 9). This behavior is quite dramatic since poly(perfluoroethers) are one of the most

20 CO$_2$-philic polymers known to date, and the PO/CO$_2$ copolymers are likely to be at least 1/100 the cost of the fluorinated materials.

The phase behavior of other oxirane/CO$_2$ copolymers was also examined. Ethylene oxide (EO) was copolymerized

25 with carbon dioxide. It was found that an EO/CO$_2$ copolymer with 103 repeat units had almost the same phase behavior (Figure 10) as a homopolymer of EO with only 16 repeat units (a EO homopolymer with 103 would be essentially insoluble in this pressure range).

Copolymers of cyclohexene oxide and CO_2 were also synthesized. One might expect that the chain would be less flexible as a result of the cyclohexane rings. Miscibility pressures for these types of copolymers (as for others) are

5.   a function of molecular weight and of incorporated carbon dioxide (as carbonate units). For example, the data in Figure 11 show that miscibility pressures increase upon increasing chain length at (relatively) constant % of carbonate, as expected. However, as shown in Figure 12,

10   the amount of carbonate required to render these copolymers "CO_2-philic" was apparently much lower than the levels in the materials in Figure 11. Figure 12 shows that copolymers with less than 10% carbonate repeats exhibited miscibility pressures below 150 atmospheres. The cloud point curves for

15   CHO-CO_2 copolymers with N=124 repeat units (8.8% carbonate) and N=88 repeat units (2.3% carbonate) showed almost the same behavior despite being different by 36 repeat units. That the CHO/CO_2 copolymers are so CO_2-philic is somewhat surprising. The data in Figure 12 may be a result of

20   increased chain flexibility upon introduction of carbonate repeats into a poly(CHO) or to unfavorable enthalpic interactions between carbonate and cyclohexyl groups.

It should be also noted that the solubility of low molecular weight polymers in carbon dioxide is affected by

25   the nature of the end groups. It was observed that mono hydroxy terminated polyethers are more soluble than a difunctional homologue with the same number of repeat units, but less soluble than an acetoxy terminated polyether (Figures 13). Again, addition of an acetate group provides

30   a superior response to addition of an alkyl group.

The phase behavior of these materials illustrates that hydrocarbons can indeed be strongly CO_2-philic without F or Si atoms incorporated therein. Furthermore, by incorporating the carbonyl group in the main chain, these
5   materials are biodegradable as well as CO_2-philic.

The above studies demonstrate that the solubility of polyethers in CO_2 is dramatically affected either by addition of acetate groups in the side chain or carbonate groups in the backbone of the polymer. Miscibility
10 pressures of polyethers modified with acetate groups decrease as the acetate contents increases, yet a point is reached where additional acetate content raises cloud point pressures. These observations are consistent with the general criteria set forth above. The oxirane/CO_2
15 copolymers were very soluble even to the point where a PO/CO_2 copolymer was more soluble than a poly(perfluoroether). It remains unclear, however, if it better to put carbonyl groups in the side chain or the backbone. Figure 14 shows that a copolymer of
20 epichlorohydrin and CO_2 with 17 repeat units and 25 % carbonate was less soluble than a poly(epichlorohydrin) with 25 repeat units modified with 45 % acetate groups. However it is not known if 25% is the optimum level of carbonate linkages in the ECH/CO_2 copolymer for maximum solubility (or
25 if 45% acetate is also optimal). In general, there is preferably a balance between the favorable entropic effects from chain flexibility and the enthalpic effects created by solute/solvent interactions.

CO₂-PHILIC VINYL POLYMERS

The polyethers and polyether/polycarbonate copolymers described above are synthesized from commodity raw materials (for example, CO_2 and oxiranes) and are hence far less expensive than fluorinated CO_2-philes. However, the polymerization mode (coordinative ring opening) does not always lend itself to easy generation of functionalized polymers. Hydrocarbons generated from simple vinyl monomers may also be polymerized from inexpensive reagents and generally are readily functionalized with a wide range of functional groups.

The criteria established in the present invention for CO_2-philes indicates that copolymers based on either ethylene or propylene will provide good candidates for CO_2-philic hydrocarbons as polymers formed from each of these monomers exhibit very low T_g and low cohesive energy density. Each of these monomers may present some synthetic difficulties, however. Free-radical copolymerization of ethylene with functional monomers (such as vinyl acetate), wherein the functional monomer is in the minority (40 mole % and below), can only occur at extreme conditions (for example, 2000 bar, and above 200°C). Burkhart, R.D.; Zutty, N.L.; J. Polym. Sci., Part A (1963), 1, 1137. Unfortunately, Ziegler-type catalysts that operate under mild conditions do not copolymerize polar monomers with ethylene or propylene (see, Odian, G.; Principles of Polymerization, 3rd Edition (1991), John Wiley & Sons, New York, Section 8-4d.). One can "mask" the polar group, however, allowing copolymerization. Xie, H-Q.; Baker, W.E.; Arshady, R.; in Desk Reference of Functional Polymers; Synthesis and Applications, Arshady, R., editor (1997), Amer. Chem. Soc.,

Washington, DC, 133.   Propylene is also somewhat
problematic, in that it can only be copolymerized (other
than with Ziegler style catalysts, which will not function
with polar monomers) cationically, possibly limiting one to
5   vinyl ethers as potential comonomers in that reaction
scheme.

        Nickel di-imine catalysts as known in the art may
be suitable to copolymerize ethylene or propylene and vinyl
acetate (for example) under mild conditions and somewhat
10   elevated pressures.

        Butadiene also presents a promising base
material/monomer for the vinyl CO_2-philes of the present
invention. In that regard, polybutadiene exhibits a very low
T_g, and also a cohesive energy density lower than that of
15   polypropylene oxide.   Butadiene is inexpensive and can be
copolymerized with a variety of vinyl monomers using free-
radical initiators, easing the synthesis of CO_2-philic
oligomers.   Free-radical polymerization of butadiene also
creates repeat units of both the 1,2 and 1,4 types, which
20   distribution desirably tends to eliminate the potential of
crystallization and raise free volume.

        Copolymerizations of butadiene and comonomers may
be conducted free-radically in solvent using butyl mercaptan
to limit the molecular weight to the desired number of total
25   repeat units (GPC, Waters 150 CV may be used to ascertain
molecular weight).

        Side chains with the various functional groups of
interest (preferably, Lewis bases) may be generated using

the strategy outlined below. Generation of carbonyl-
containing ester-functional side chains with a 1 or 2 atom
spacer, for example, is relatively straightforward. Vinyl
acetate may be copolymerized with butadiene to generate the
5   ester-functional side chain with a 1-atom spacer. The
mole % of the comonomer is relatively easy to manipulate and
to ascertain (via ^{1}H NMR). Generation of the analog with a
2-atom spacer is readily accomplished via (a) free-radical
copolymerization of butadiene with acrolein, followed by
10   (b) reduction of the aldehyde side chains to CH_2OH, and then
(c) reaction of the hydroxyl group with acetoyl chloride.
Given the low molecular weight of the precursor oligomers
and the innate high yield of the proposed reactions, near
quantitative conversion of the original aldehyde side groups
15   to acetate may be accomplished. Characterization may be
performed using ^{1}H NMR (tracking the signals resulting from
the C(O)-H proton, the CH_2-O protons, and ultimately those
of the ester group). FT-IR can be used to qualitatively
follow the change from aldehyde to alcohol to ester.

20   Analogs with phosphonyl groups as side chains are
readily prepared via (a) base-catalyzed hydrolysis of the
vinyl acetate/butadiene copolymer described above, followed
by (b) reaction with chloro-diethyl phosphonate (Aldrich)
with a base catalyst to generate the analog with a 1-atom
25   spacer. An analog with a 2-atom spacer is prepared, for
example, via a reduced acrolein copolymer discussed above,
followed again by reaction with the chloro diethyl
phosphonate. By employing common precursors for both the
carbonyl and phosphonyl analogs, one can eliminate molecular
30   weight and compositional distributions as variables in the
phase behavior analysis. As in the case of the carbonyl
variants, the proposed reactions can proceed to near

quantitative yield, and are easily followed using ^{1}H and ^{31}P NMR.

        A number of viable routes are available for the preparation of a tertiary amine-containing oligomer with, for example, a 1-atom spacer. For example, the reduced acrolein copolymer described above (with side chains of - CH_2-OH) can be tresylated, then reacted with dimethyl amine to form the required model CO_2-phile. As discussed above, this route is advantageous because it eliminates effects arising from variances in molecular weight and composition distribution (through use of common precursors). A simpler method, however, involves (a) copolymerization of butadiene with N,N dimethyl acrylamide, followed by (b) reduction of the amide groups to, fro example, CH_2-$N(CH_3)_2$ using lithium aluminum hydride. As before, such a reaction on a low molecular weight, highly soluble oligomer may be nearly quantitative. The extent of the reduction is readily followed via ^{1}H NMR or FT-IR.

        In several studies of the present invention, copolymers of vinyl acetate (VA) and ethyl vinyl ether (EVE) with varying chain length and vinyl acetate composition were prepared free radically. These monomers were chosen, in part, for ease of synthesis. The amount of vinyl acetate incorporated depended on the initial amount of vinyl acetate that was used to charge the reactor, while chain length was a function of the amounts of initiator and chain transfer agent employed. Characterization was done using ^{1}H NMR from the peaks at 5.03 (-CH from vinyl acetate) and 3.43 (-CH_3 from ethyl vinyl ether). The solubility of the polymers in liquid CO_2 was studied at 22 °C.

Ethyl vinyl ether is a synthetically tractable yet non-ideal choice for monomer 1, as it exhibits a higher Tg (~ 230K) and cohesive energy density than optimally desired. This is shown clearly in Figure 15, wherein a homopolymer of

5   ethyl vinyl ether of only 20 repeat units exhibited miscibility pressures above 260 bar for concentrations above 1 weight percent. By contrast, a 25 repeat-unit homopolymer of propylene oxide exhibited miscibility pressures well below 200 bar, and homopolymers of vinyl acetate of

10   significantly longer chains lengths exhibited miscibility pressures in the same general pressure range (Figure 15). Nevertheless, the use of EVE was instructive in the pursuit of the design of non-fluorous CO_2-philes via balancing the contributions of monomer 1 and monomer 2.

15   Figure 16 shows the phase behavior of copolymers of EVE and vinyl acetate wherein the total chain length of the copolymers was 70 (+/- 5) repeats. As hypothesized, adjustment of vinyl acetate (monomer 2 in the scheme of Figure 1) content allowed for lower miscibility pressures of

20   the copolymer than either of the homopolymers (note that cloud point pressures for a homopolymer of EVE of 70 repeats are above the pressure limits of the equipment). This trend was repeated for chains of 90 repeats (+/- 5), as shown in Figure 17. From the data in Figures 16 and 17, it can be

25   estimated that a vinyl acetate content of 25-30% will provide the lowest miscibility pressures for this class of copolymer. Unfortunately, it is difficult to a priori predict the optimal monomer 2 (in this case vinyl acetate) content of the copolymer. The above studies of ether-

30   carbonate copolymers, illustrate that the ideal carbonate content varied significantly as the type of oxirane varied from ethylene oxide to propylene oxide to cyclohexene oxide.

At relatively constant vinyl acetate content, changing molecular weight produces the expected effect (Figure 18), wherein increasing chain length increased miscibility pressures.

5   The results for vinyl copolymers can be greatly improved (that is, lower miscibility pressures observed) in copolymers wherein the Tg and cohesive energy density of polymers of monomer 1 were lower than that of poly(ethyl vinyl ether). For example, either butadiene or isobutylene 10   are effective choices for monomer 1.

CO$_2$-PHILIC POLY(ETHER-ESTERS)

        Poly(ether-ester) copolymers of the present invention can be synthesized by reacting, for example, a dihydroxy polyalkylene oxide (a polyether with a hydroxy 15   group at each end) with a di-acid, a di-alkyl ester, or a di-acid halide at elevated temperature (generally, above 65°C, but below 200°C), using vacuum to remove the byproduct (water or alcohol). Alternatively, a base can be added in the case of the di-acid halide (byproduct is HCl). These 20   synthetic techniques and others for synthesizing the poly(ether-ester) copolymers of the present invention are well known to those skilled in the art. Like the poly(ether-carbonate) groups discussed above, the poly(ether-ester) copolymers of the present invention 25   include a Lewis base (carbonyl group) in the copolymer backbone.

SYNTHESIS OF CO_2-PHILIC ANALOGS

In general, compounds not soluble or miscible in CO_2 (that is, CO_2-phobic compounds) can be made more soluble or miscible in CO_2 by synthesizing "CO_2-philic analogs" of

5   such compounds incorporating one or more CO_2-philic groups. Processes and reactions that are normally not possible in CO_2, are thereby made possible. For example, surfactants, chelating agents and reactants for use in carbon dioxide can be synthesized in this manner. <u>See</u>, for example, U.S.

10   Patent Application Serial No. 09/106,480; U.S. Patent No. 5,641,887; and U.S. Patent No. 5,872,257.

Figure 19 sets forth a general formula for such compounds. As illustrated in Figure 19, CO_2-philic analogs of CO_2-phobic compounds include generally a CO_2-phobic group

15   corresponding to the underlying CO_2-phobic compound and a CO_2-philic segment including at least one CO_2-philic group (g is an integer of at least one in Figure 19). The CO_2-phobic group and the CO_2-philic group(s) are preferably covalently attached via a spacer or connector group. As

20   known from previous work with fluorinated and silicon CO_2-philes, the compounds of Figure 19 can be prepared from the CO_2-philes of the present invention by preferably synthesizing such CO_2-philes with a reactive terminal functionality or reactive functional group such as a

25   hydroxyl group. This terminal functional group of the CO_2-phile is preferably reactive with a functional group on the CO_2-phobic compound. The reaction between the terminal functional groups of the CO_2-phobic compound and the CO_2-phile results in the spacer or connector group. Many

30   such functional groups are know to those skilled in the art. The functional groups of the CO_2-phobic compound and the

CO_2-phile(s) preferably results in a spacer group that enhances or does not substantially reduce the CO_2-philic nature of the compound of Figure 19. Spacer groups may, for example, include divalent forms of an ester, a keto, an
5   ether, a thio, an amido, an amino, a polyalkylene oxide, a phosphato, a sulfonyl, a sulfate, an ammonium, an alkylene or combinations thereof.

       An end group (typically not a reactive functionality unless difunctionality is desired) at the
10   other terminus of the CO_2-philic compounds of the present invention can be almost any group. However, such end groups preferably enhance or do not substantially reduce the CO_2-philic nature of the CO_2-philic analog of Figure 19. Preferred end groups include, but are not limited to H,
15   alkyl, alkenyl or ether groups.

       Surfactants may, for example, be synthesized using these materials. Copolymerizations of oxiranes and CO_2 using sterically hindered alkoxy aluminum catalysts are "living" in character, and thus block copolymer synthesis is
20   relatively straightforward. For example, one can generate a water-soluble surfactant by copolymerizing EO and CO_2, then removing the CO_2 before all of the EO is polymerized (via flashing). Conversely, one can begin a homopolymerization of EO, then added CO_2 (via simply opening a valve) part way
25   through the polymerization. These techniques produce a carbonate-ether diblock material that does lowers interfacial tension of water. Generating an optimized CO_2-philic surfactant with a poly(ether-carbonate) CO_2-philic group simply requires, for example, (a) identifying the most
30   appropriate carbonate (for example, CHO, EO- or PO-based), then determining the correct ratio of carbonate/ether block

length to produce a CO_2-soluble surfactant. All the optimizing determinations are readily made experimentally.

Previous work on design of CO_2-philic surfactants has also identified both linear ammonium carboxylates and branched sodium sulfonates (for example, AOT) as useful structures. See Johnston, K.P.; Harrison, K.L.; Clarke, M.J.; Howdle, S.; Heitz, M.P.; Bright, F.V.; Carlier, C.; Randolph, T.W.; Science (1996), 271, 624; and Hoefling, T.A.; Enick, R.M.; Beckman, E.J.; J. Phys. Chem. (1991), 95, 7127.

To synthesize CO_2-philic analogs from the vinyl CO_2-philic compositions of the present invention, hydroxy-terminal oligomers may, for example, generated by replacing the conventional initiator (AIBN) with a hydroxy-functional analog, and by replacing the butyl mercaptan chain transfer agent with a hydroxy-thiol analog (Aldrich). See Okaya, T.; Sato, T.; in Polyvinyl Alcohol - Developments, Finch, C.A., editor (1992), John Wiley & Sons, New York, Chapter 5. This technique could also be used to generate surfactants directly by employing an inifer surfactant as described by Guyot and Vidal. See Guyot, A.; Vidal, F.; Polym. Bull. (1995), 34, 569 (c) Vidal, F.; and Hamaide, T.; Poym. Bull. (1995), 35, 1.

Ammonium carboxylate surfactants may, for example, be synthesized by reaction of the hydroxy-terminated oligomers with maleic anhydride, followed by neutralization with ammonium hydroxide. AOT analogs may generated via reaction of two equivalents of the hydroxy-oligomer with fumaryl chloride, followed by sulfonation with sodium hydrogen sulfite.

Experimental

Materials

All synthesis were carried out in purified argon atmosphere. Monomers and solvents were purified as described previously. Ethylene oxide was used as received. Epichlorohydrin (Aldrich Chemicals, Milwaukee, WI) was distilled under reduced pressure. Carbon dioxide and argon (both 99.99 % purity from Praxair, Pittsburgh, PA) were passed through high pressure purifiers before use.

Vinyl acetate (VA) and ethyl vinyl ether (EVE) were obtained from Aldrich Chemical Company. Vinyl acetate was purified by passage through an inhibitor-sorbing column (Aldrich) to remove hydroquinone. Ethyl vinyl ether was distilled under an argon atmosphere. The initiator, 2,2′ azoisobutyronitrile, was recrystallized twice from ether. Poly(ethyl vinyl ether), 20 repeat units, was generously donated by BASF Corporation (Ludwigshafen, GER).

All other chemicals were obtained from Aldrich Chemicals and used as received, unless otherwise noted.

Synthesis of Acetate Functionalized Poly(Epichlorohydrin)

Low molecular weight poly(epichlorohydrin) was used as the starting material to produce acetate-modified polymers with varying acetate content. In a typical polymerization reaction, boron trifluoride diethyl ether (1.5 ml, 0.0118 moles) was added dropwise to a solution of

20 ml epichlorohydrin (0.2557 moles) in 44 ml of toluene
over 30 minutes at room temperature. After 4 hours the
catalyst was deactivated with aqueous NaOH, and the organic
phase was separated and dried over $CaCl_2$. The solvent was
5   removed under reduced pressure at 50 °C and the polymer
analyzed using NMR and GPC. Poly(epichlorohydrin) with 7
repeat units was produced with a yield of 90-95%. To
generate higher molecular weight polymer (e. g. 25 repeat
units), methylaluminoxane (kindly supplied by Akzo Nobel)
10   was used as the initiator. The polymerization was stopped
with methanolic hydrochloric acid and the polymer solution
was filtered and processed as above.

     For modification with acetate groups, the polymer
was reacted with potassium acetate using a phase transfer
15   catalyst (benzyltrimethyl ammonium chloride) in toluene
(Figure 2). The reaction mixture was heated to 50-80 °C for
24 hours. The solution was allowed to cool to room
temperature and the remaining catalyst and potassium acetate
were removed by filtration. The polymer solution was washed
20   rapidly three times with cold water to remove any unreacted
potassium acetate, then dried with magnesium sulfate. The
solvent was removed under reduced pressure. The amount of
acetate incorporated was determined by ^{13}C NMR from the
ratio of the CH_2Cl peak at 43-45 ppm and CO peak from
25   acetate at 170-171 ppm. Maximum degree of modification was
45%.

Synthesis of Poly(Glycidyl Acetate)

     Polymers containing only acetate groups in the
side chain were synthesized by polymerization of glycidyl

acetate in a similar manner as epichlorohydrin, using a sterically hindered aluminum catalyst of the type $((H_5C_6)_3C-O)_2-Al-O-CH(CH_3)_2$. The glycidyl acetate was synthesized according to known procedures described in the

5 literature. See Davies, A. G.; Alwyn, G.; Hawari, J.A.-A.; Muggleton, B.; Tse, M.-W. J. Chem. Soc. Perkin Trans., 2, 1981, 1132.

Synthesis of Catalysts for Oxirane/CO₂ Copolymerization

These catalysts were synthesized under argon, in

10 glass flasks that were heated to 200°C and then evacuated and flushed with inert gas three times. The catalysts used for the copolymerization of propylene oxide and carbon dioxide were monofunctional (**1**) or difunctional (**2**) sterically-hindered aluminum alkoxides or phenoxides

15 (Figure 6). First, triisobutylaluminum was reacted with tri(phenyl)methanol or a sterically hindered phenol, then with an appropriate alcohol or glycol. The ^{27}Al-NMR spectra of the catalysts showed that the sterically hindered aluminum catalysts exhibited essentially only

20 pentacoordination. If Al atom was hexacoordinated then then ^{27}Al NMR would also show a peak at 0 ppm but the pentacoordinated species only showed a peak at appoximately 60 ppm. These NMR results suggest that the catalysts exhibited one species of active site (unlike previously

25 reported catalysts for the polymerization of oxiranes and carbon dioxide); which perhaps explains the living character of the polymerizations subsequently observed.

In a typical experiment 10 mL tri-isobutyl aluminum (TIBA), as a 1.0 molar solution in toluene, was

reacted with 5.207g (0.02 mol) tri(phenyl)methanol at 40°
for 2-4 hours and then 0.77 mL (0.01 mol) isopropanol was
added dropwise, and the mixture was stirred for two hours.
The suspension of catalyst in toluene was then cooled to

5   room temperature, the solvent was removed with a syringe and
the catalyst washed twice with a small amount of dried
toluene.   The remaining solvent was then removed under
vacuum at 50°C. The aluminum catalysts with sterically
hindered phenoxide substituents were used as a toluene

10   solution.

Copolymerization of Cyclic Ethers and Carbon Dioxide.

Copolymerization of cyclic ethers and carbon
dioxide was performed in either a 25mL or 35mL high-pressure
reactor equipped with magnetic stirrer and pressure and

15   temperature indicators. Prior to the experiment the reactor
was heated to 200°C, evacuated, and then cooled to room
temperature under an argon blanket. The desired amount of
aluminum catalyst was introduced to the reactor under an
argon blanket, the reactor was sealed and evacuated for 15-

20   20 minutes, then finally flushed with argon. The soluble
aluminum compounds were used as a toluene solution and
introduced with a syringe. The oxirane was added alone using
a syringe, or as a mixture with CO_2 using a high-pressure
syringe pump (High Pressure Equipment Co.). After injection

25   of the reagents, the reactor was isolated and heated to the
prescribed temperature (40-60°C). After the desired time the
pressure was slowly released, and the reaction was
terminated with methanolic hydrochloric acid. The polymer
solution was filtered, processed and analyzed.   The amount

30   of carbonate incorporated into the polymer was determined
from the integrals of the ether protons peaks at

approximately 3.4-3.6 ppm and the carbonate bound protons at
4.8 ppm from ^{1}H-NMR. The reaction of cyclic ethers and
carbon dioxide produced copolymers inclduding both ether and
carbonate linkages.

5 **Synthesis of Acetate Terminated Poly(propylene oxide)**

Poly(propylene) oxide (monobutyl ether) with 7 or
21 repeat units was reacted with an excess of acetyl
chloride in toluene for 24 hours. The residual reactant and
solvent were subsequently removed under vacuum.

10 **Synthesis of poly(vinyl acetate)**

A three-neck glass flask evacuated with argon was
charged with 10 ml (0.1085 moles) of vinyl acetate, 20 ml of
toluene, and 0.228 g of 2,2' azoisobutyronitrile (0.00139
moles). The reaction mixture was then heated to 60 °C for 4
15 hours. n-Butyl mercaptan was used as chain transfer agent;
amounts employed varied as the desired molecular weight
varied.

Synthesis of poly(ethyl vinyl ether)

A three-neck glass flask evacuated with argon was
20 charged with 10 ml (0.1279 moles) of ethyl vinyl ether and
20 ml of toluene. Boron trifluoride diethyl etherate (0.250
ml, 0.0016 moles) was added dropwise to the EVE solution,
which was kept at 20 °C throughout the reaction. The
reaction was allowed to proceed for 24 hours and then was
25 terminated with dilute aqueous sodium hydroxide. The
resulting mixture was extracted with ether to remove the

polymer and the ether solution was re-washed with aqueous
dilute sodium hydroxide to remove the residual catalyst
residue. The ether solution was then dried with magnesium
sulfate and filtered.

5   **Synthesis of poly(vinyl acetate co-ethyl vinyl ether)**

          In a typical reaction, a stainless steel reactor
(50 cm^3, manufactured at the University of Pittsburgh) was
charged with 10 ml of ethyl vinyl ether (0.1046 moles), 2 ml
of vinyl acetate (0.0217 moles), and 0.228 g of 2,2'
10   azobis(isobutyrnitrile) (0.00139 moles). The reactor was
sealed and then submersed in an oil bath. The temperature
in the oil bath was raised to 60 °C and the reaction was
allowed to proceed at the vapor pressure of the monomer
mixture for 4 hours. The polymer was recovered with
15   methanol. The solvent was subsequently removed under
reduced pressure.

Phase Behavior Measurements

          The phase behavior of the copolymers was measured
using a high-pressure, variable-volume view cell (D.B.
20   Robinson & Assoc.). This cell is a quartz tube containing a
floating piston. The entire tube assembly is encased in a
windowed, stainless steel vessel capable of supporting
pressures up to 500 bar. A known amount of solute was added
to the view-cell chamber above the piston. The chamber was
25   then sealed and charged with liquid CO_2. The pressure on
the sample was altered at constant composition via injection
of silicone oil, which moved the floating piston higher in
the quartz tube. Initially, the pressure was raised to the

point where a clear, single-phase solution was obtained. The phase boundary (cloud point, or miscibility) was found subsequently by lowering the pressure until the solution became cloudy.

5   **Analyses**

All ^{1}H NMR spectra were recorded on a Bruker DMX 300 instrument where the polymers were dissolved in d-chloroform with tetramethylsilane used as the internal reference.   The ^{27}Al-NMR   (75.468 MHz) spectra of the
10   catalysts were recorded as known in the art. Molecular weights of the product polymers were determined using a Waters 150CV gel permeation chromatograph, equipped with 10^4, 10^3, 500 and 100 A ultrastyragel columns. THF was used as eluent and calibration was performed using polystyrene
15   standards. IR spectra were recorded on a Mattson Genesis II FTIR. Phase behavior of the polymers was studied in a variable volume high pressure view cell, equipped with stirrer and temperature and pressure controllers.

       Molecular weight and the molecular weight
20   distribution of the polymers were measured using a Waters 150 CV gel permeation chromatograph, equipped with 10^4, 10^3, 500 and 100 Å Ultrastyragel columns.

       Although the present invention has been described in detail in connection with the above examples, it is to be
25   understood that such detail is solely for that purpose and that variations can be made by those skilled in the art without departing from the spirit of the invention except as it may be limited by the following claims.

WHAT IS CLAIMED IS:

1.   A method of synthesizing a CO_2-philic analog
of a CO_2-phobic compound that is more CO_2-philic than the
CO_2-phobic compound, comprising the step of:

reacting the CO_2-phobic compound with a CO_2-philic compound,
wherein the CO_2-philic compound is a polyether substituted
with at least one side group including a Lewis base, a
poly(ether-carbonate), a poly(ether-carbonate) substituted
with at least one side group including a Lewis base, a vinyl
polymer substituted with at least one side groups including
a Lewis base, a poly(ether-ester) or a poly(ether-ester)
substituted with at least one side groups including a Lewis
base to create the CO_2-philic analog.

2.   The method of claim 1 wherein the CO_2-philic
compound is a polyether substituted with at least one side
group including a Lewis base, a poly(ether-carbonate), a
poly(ether-carbonate) substituted with at least one side
group including a Lewis base, or a vinyl polymer substituted
with at least one side group including a Lewis base.

3.   The method of claim 1 wherein the CO_2-philic
contains no F or Si atoms.

4.   The method of claim 1 wherein the CO_2-philic
compound is a polyether copolymer including the repeat units

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, and R^{12} are, independently, the same or different, H, an alkyl group, $-(R^{22'})_z R^{22}$, or R^4 and R^6 form of carbon cyclic chain of 3 to 8 carbon atoms, wherein $R^{22'}$ is an alkylene group and z is 0 or 1, and R^{22} is a Lewis base group, wherein at least one of R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, and R^{12} is $-(R^{22'})_z R^{22}$, wherein, i, j, k, l, m, and n are independently, the same or different, 0, 1 or 2, at least one of i, j, and k being 1 or 2 and at least one of l, m, and being 1 or 2, and x and y are integers.

5. The method of claim 4 wherein R^{22} is $-O-C(O)-R^{23}$, $-C(O)-R^{23}$, $-O-P(O)-(O-R^{23})_2$, or $-NR^{23}R^{23'}$, wherein R^{23} and $R^{23'}$ are independently, the same or different, an alkyl group.
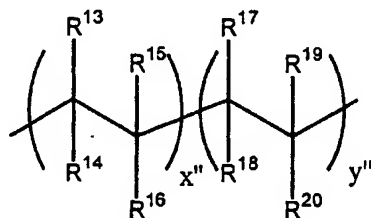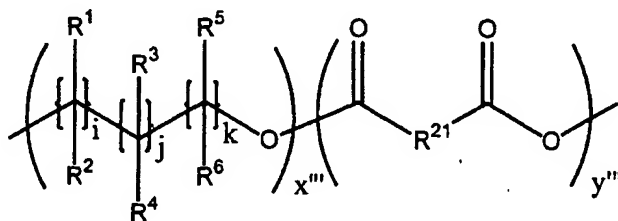
6. The method of claim 4 wherein $R^{22'}$ is $-(CH_2)_a-$ and a is an integer between 0 and 5.

7. The method of claim 6 wherein a is 1 or 2 and i is 0, j is 1, k is 1, l is 0, m is 1 and n is 1

8. The method of claim 7 wherein R^3, R^4, R^5, R^9, R^{10}, and R^{11} are H, R^6 is an alkyl group and R^{12} is $-(CH_2)_a-R^{22}$.

9. The method of claim 8 wherein R^{22} is $O-C(O)-R^{23}$, $-C(O)-R^{23}$, $-O-P(O)-(O-R^{23})_2$, or $-NR^{23}R^{23\prime}$, wherein R^{23} and $R^{23\prime}$ are independently, the same or different, an alkyl group.

10. The method of claim 8 wherein R^{22} is $-O-C(O)-R^{23}$.

11. The method of claim 10 wherein R^{23} is a methyl group.

12. The method of claim 4 wherein the polyether copolymer contains no F or Si atoms.

13. The method of claim 1 wherein the CO_2-philic compound is a poly(ether-carbonate) copolymer including the repeat units:

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, and R^{12} are, independently, the same or different, H, an alkyl group, $-(R^{22\prime})_zR^{22}$, or R^4 and R^6 form of carbon cyclic chain of 3 to 8 carbon atoms, wherein $R^{22\prime}$ is an alkylene group and z is 0 or 1, and R^{22} is a Lewis base group, wherein, i, j, k, l, m, and n are independently, the same or different, 0, 1 or 2, at least one of i, j, and k being 1 or 2 and at

least one of l, m, and being 1 or 2, and x' and y' are integers.

14.   The   method   of   claim 13   wherein R^{22} is $-O-C(O)-R^{23}$, $-C(O)-R^{23}$, $-O-P(O)-(O-R^{23})_2$, or $-NR^{23}R^{23'}$, wherein R^{23} and $R^{23'}$ are independently, the same or different, an alkyl group.

15.   The   method   of   claim 14   wherein $R^{22'}$ is $-(CH_2)_a-$ and a is an integer between 0 and 5.

16.   The method of claim 15 wherein a is 1 or 2.

17.   The method of claim 13 wherein i is 0, j is 1, k is 1, l is 0, m is 1 and n is 1 and R^3, R^4, R^5, R^9, R^{10}, and R^{11} are H, R^6 is an alkyl group and R^{12} is an alkyl group.

18.   The   method   of   claim 13   wherein   the poly(ether-carbonate) copolymer contains no F or Si atoms.

19.   The   method   of   claim 1 wherein the vinyl polymer is a copolymer including the repeat units:

wherein R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, and R^{20} are, independently, the same or different, H, an alkyl group, an alkenyl group, $-O-R^{24}$, $-(R^{22'})_z R^{22}$, wherein, $R^{22'}$ is an alkylene group, R^{22} is a Lewis base group and z is 0 or 1, R^{24} is an alkyl group, wherein at least one of R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, and R^{20} is $-(R^{22'})_z R^{22}$, and x″ and y″ are integers.

20. The method of claim 19 wherein $R^{22'}$ is $-(CH_2)_a-$ and a is an integer between 0 and 5.
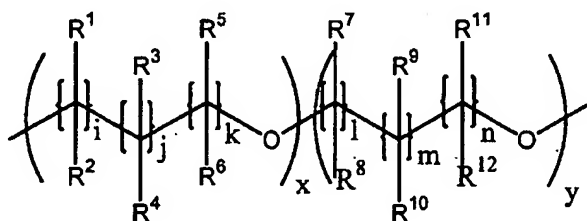
21. The method of claim 20 wherein a is 1 or 2 and R^{22} is $-O-C(O)-R^{23}$, $-C(O)-R^{23}$, $-O-P(O)-(O-R^{23})_2$, or $-NR^{23}R^{23'}$, wherein R^{23} and $R^{23'}$ are independently, the same or different, an alkyl group.

22. The method of claim 21 wherein R^{22} is $-O-C(O)-R^{23}$.

23. The method of claim 19 wherein the vinyl copolymer contains no F or Si atoms.

24. The method of claim 1 wherein the CO_2-philic compound is a poly(ether-ester) copolymer including the repeat units

wherein R^1, R^2, R^3, R^4, R^5 and R^6 are, independently, the same or different, H, an alkyl group, $-(R^{22'})_z R^{22}$, or R^4 and R^6 form of carbon cyclic chain of 3 to 8 carbon atoms, wherein z is 0 or 1, $R^{22'}$ is an alkylene group and R^{22} is a lewis base group, wherein, i, j and k are independently, the same or different, 0, 1 or 2, at least one of i, j, and k being 1 or 2, R^{21} is an alkylene group, a cycloalkylene group, a difunctional ester group, or a difunctional ether group, and x''' and y''' are integers.

25. The method of claim 24 wherein at least one of R^1, R^2, R^3, R^4, R^5 and R^6 is $-(R^{22'})_z R^{22}$, and R^{22} is $-O-C(O)-R^{23}$, $-C(O)-R^{23}$, $-O-P(O)-(O-R^{23})_2$, or $-NR^{23}R^{23'}$, wherein R^{23} and $R^{23'}$ are independently, the same or different, an alkyl group.

26. The method of claim 25 wherein $R^{22'}$ is $-(CH_2)_a-$ and a is an integer between 0 and 5.

27. The method of claim 26 wherein a is 1 or 2 and i is 0, j is 1, and k is 1.

28. The method of claim 24 wherein R^{22} is $-O-C(O)-R^{23}$, $-C(O)-R^{23}$, $-O-P(O)-(O-R^{23})_2$, or $-NR^{23}R^{23'}$, wherein R^{23} and $R^{23'}$ are independently, the same or different, an alkyl group.

29. The method of claim 27 wherein R^{22} is $-O-C(O)-R^{23}$.

30. A surfactant for use in carbon dioxide, the surfactant comprising a CO_2-phobic group covalently linked

60

to a CO_2-philic segment, wherein the CO_2-philic segment includes a polyether substituted with at least one side group including a Lewis base, a poly(ether-carbonate), a poly(ether-carbonate) substituted with at least one side group including a Lewis base, a vinyl polymer substituted with at least one side group including a Lewis base, a poly(ether-ester) or a poly(ether-ester) substituted with at least one side group including a Lewis base.

31. The surfactant of claim 30 wherein the polyether is a polyether copolymer including the repeat units

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, and R^{12} are, independently, the same or different, H, an alkyl group, $-(R^{22'})_z R^{22}$, or R^4 and R^6 form of carbon cyclic chain of 3 to 8 carbon atoms, wherein $R^{22'}$ is an alkylene group and z is 0 or 1, and R^{22} is a Lewis base group, wherein at least one of R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, and R^{12} is $-(R^{22'})_z R^{22}$, wherein, i, j, k, l, m, and n are independently, the same or different, 0, 1 or 2, at least one of i, j, and k being 1 or 2 and at least one of l, m, and being 1 or 2, and x and y are integers.

32. The surfactant of claim 31 wherein R^{22} is $-O-C(O)-R^{23}$, $-C(O)-R^{23}$, $-O-P(O)-(O-R^{23})_2$, or $-NR^{23}R^{23'}$, wherein

R^{23} and $R^{23'}$ are independently, the same or different, an alkyl group.

33. The surfactant of claim 32 wherein $R^{22'}$ is $-(CH_2)_a-$ and a is an integer between 0 and 5.

34. The surfactant of claim 30 wherein the poly(ether-carbonate) copolymer includes the repeat units:
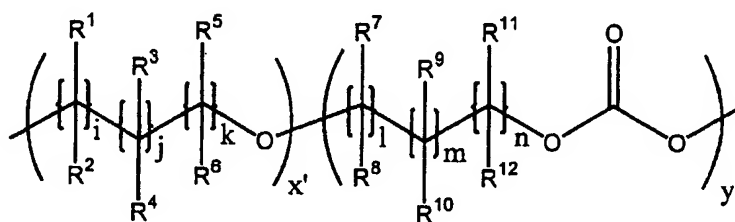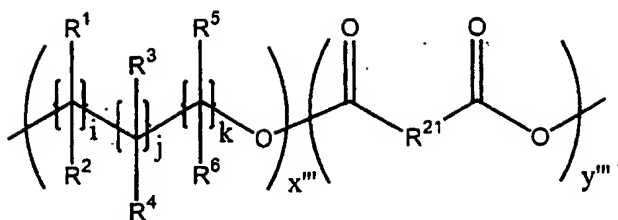

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, and R^{12} are, independently, the same or different, H, an alkyl group, $-(R^{22'})_z R^{22}$, or R^4 and R^6 form of carbon cyclic chain of 3 to 8 carbon atoms, wherein $R^{22'}$ is an alkylene group and z is 0 or 1, and R^{22} is a Lewis base group, wherein, i, j, k, l, m, and n are independently, the same or different, 0, 1 or 2, at least one of i, j, and k being 1 or 2 and at least one of l, m, and being 1 or 2, and x' and y' are integers.

35. The surfactant of claim 34 wherein R^{22} is $-O-C(O)-R^{23}$, $-C(O)-R^{23}$, $-O-P(O)-(O-R^{23})_2$, or $-NR^{23}R^{23'}$, wherein R^{23} and $R^{23'}$ are independently, the same or different, an alkyl group.

36. The surfactant of claim 36 wherein $R^{22'}$ is $-(CH_2)_a-$ and a is an integer between 0 and 5.

37. The surfactant of claim 30 wherein the vinyl polymer is a copolymer including the repeat units:
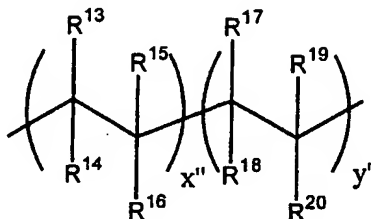
wherein R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, and R^{20} are, independently, the same or different, H, an alkyl group, an alkenyl group, $-O-R^{24}$, $-(R^{22'})_z R^{22}$, wherein, $R^{22'}$ is an alkylene group, R^{22} is a Lewis base group and z is 0 or 1, R^{24} is an alkyl group, wherein at least one of R^{13}, R^{14}, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, and R^{20} is $-(R^{22'})_z R^{22}$, and x'' and y'' are integers.

38. The surfactant of claim 37 wherein $R^{22'}$ is $-(CH_2)_a-$ and a is an integer between 0 and 5.

39. The surfactant of claim 38 wherein a is 1 or 2 and R^{22} is $-O-C(O)-R^{23}$, $-C(O)-R^{23}$, $-O-P(O)-(O-R^{23})_2$, or $-NR^{23}R^{23'}$, wherein R^{23} and $R^{23'}$ are independently, the same or different, an alkyl group.

40. The surfactant of claim 39 wherein R^{22} is $-O-C(O)-R^{23}$.

41. The surfactant of claim 30 wherein the CO_2-philic compound is a poly(ether-ester) copolymer including the repeat units

$$\left(\left[\underset{\underset{R^2}{|}}{\overset{\overset{R^1}{|}}{\underset{i}{C}}}\right]\left[\underset{\underset{R^4}{|}}{\overset{\overset{R^3}{|}}{\underset{j}{C}}}\right]\left[\underset{\underset{R^6}{|}}{\overset{\overset{R^5}{|}}{\underset{k}{C}}}\right]O\right)_{x'''}\left(\overset{\overset{O}{||}}{C}-R^{21}-\overset{\overset{O}{||}}{C}-O\right)_{y'''}$$

wherein R^1, R^2, R^3, R^4, R^5 and R^6 are, independently, the same or different, H, an alkyl group, $-(R^{22'})_zR^{22}$, or R^4 and R^6 form of carbon cyclic chain of 3 to 8 carbon atoms, wherein z is 0 or 1, $R^{22'}$ is an alkylene group and R^{22} is a lewis base group, wherein, i, j and k are independently, the same or different, 0, 1 or 2, at least one of i, j, and k being 1 or 2, R^{21} is an alkylene group, a cycloalkylene group, a difunctional ester group, or a difunctional ether group, and x''' and y''' are integers.

42. The surfactant of claim 41 wherein at least one of R^1, R^2, R^3, R^4, R^5 and R^6 is $-(R^{22'})_zR^{22}$, the lewis base group is $O-C(O)-R^{23}$, $-C(O)-R^{23}$, $-O-P(O)-(O-R^{23})_2$, or $-NR^{23}R^{23'}$, wherein R^{23} and $R^{23'}$ are independently, the same or different, an alkyl group.

43. The surfactant of claim 42 wherein $R^{22'}$ is $-(CH_2)_a-$ and a is an integer between 0 and 5.

44. The surfactant of claim 30 wherein the CO_2-phobic group is H, a carboxylic acid group, a hydroxy group, a phosphato group, a phosphato ester group, a sulfonyl group, a sulfonate group, a sulfate group, a branched or straight chained polyalkylene oxide group, an amine oxide group, an alkenyl group, a nitryl group, a glyceryl group, an ammonium, an alkyl ammonium, an aryl

group unsubstituted or substituted with an alkyl group or an alkenyl group, or a carbohydrate unsubstituted with an alkyl group or an alkenyl group.

45. The surfactant of claim 30 wherein the CO_2-phobic group includes at least one ion selected from the group of H^+, Na^{+2}, Li^+, K^+, NH_4^+, Ca^{+2}, Mg^{+2}, Cl^-, Br^-, I^-, mesylate and tosylate.

46. A chelating agent for use in carbon dioxide, the chelating agent comprising a CO_2-phobic chelating group covalently linked to a CO_2-philic segment, wherein the CO_2-philic segment includes a polyether substituted with side groups including a Lewis base, a poly(ether-carbonate), a poly(ether-carbonate) substituted with side groups including a Lewis base, a vinyl polymer substituted with side groups including a Lewis base, or a poly(ether-ester).

47. The chelating agent of Claim 46 wherein the chelating group is a polyaminocarboxylic acid group, a thoicarbamate group, a dithoicarbamate group, a thiol group, a dithiol group, a picolyl amine group, a bis(picolyl amine) group or a phosphate group.

48. A method of synthesizing a CO_2-philic copolymer comprising the step of copolymerizing at least two monomers, wherein a polymer formed from homopolymerization of one of the monomers has a T_g of less than approximately 250 K and a steric factor less than approximately 1.8, at least one of the monomers results a Lewis base group in the copolymer, and the resultant CO_2-phile does not contain both hydrogen bond donors and acceptors.

49. The method of claim 48 wherein a Lewis base group is within the monomer backbone.

50. The method of claim 48 wherein the Lewis group is a pendant group from the backbone of the at least one monomer.

51. The method of claim 50 wherein the Lewis base group is separated from the CO_2-phile backbone by 0 to 5 atoms.

52. The method of claim 51 wherein the Lewis base group is separated from the CO_2-phile backbone by 1 to 2 atoms.

53. The method of claim 48 wherein the CO_2-phile includes no F or Si atoms.

54. The method of claim 48 wherein the copolymer has less than 400 repeat units.

55. The method of claim 48 wherein the copolymer has less that 200 repeat units.

56. The method of claim 48 wherein the copolymer between 5 and 50 repeat units.

57. The method of claim 48 wherein repeat units of the copolymer including the Lewis base are in the range of 1 to 50 percent of all of the repeat units.

58. The method of claim 48 wherein repeat units of the copolymer including the Lewis base are in the range of 5 to 35 percent of all of the repeat units.

59. The method of claim 48 wherein repeat units of the copolymer including the Lewis base are in the range of 10 to 25 percent of all of the repeat units.

60. The method of claim 48 a first monomer is chosen such that a polymer formed from homopolymerization of the first monomer has a T_g of less than approximately 250 K and a steric factor less than approximately 1.8 and a second and different monomer results a Lewis base group in the copolymer.

61. A method of synthesizing a CO_2-phile comprising the step of copolymerizing carbon dioxide and at least one oxirane.

62. The method of claim 61 wherein the oxirane is ethylene oxide, propylene oxide cyclohexene oxide, or epichlorohydrin.
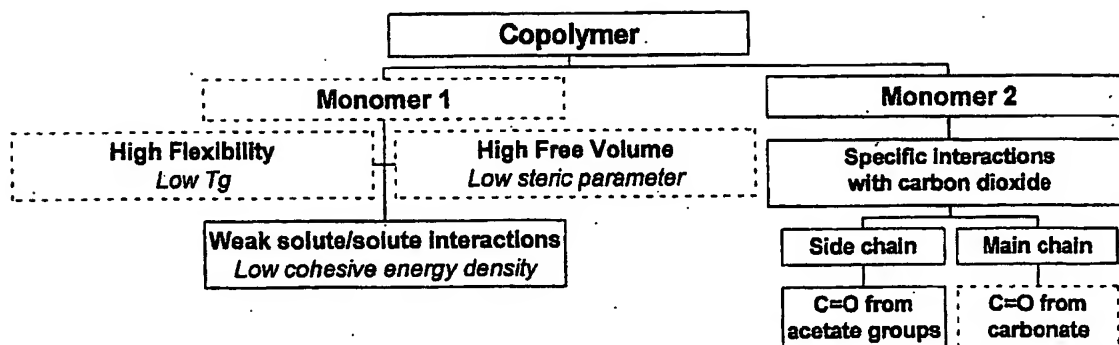
Figure 1. CO_2 –philic material design
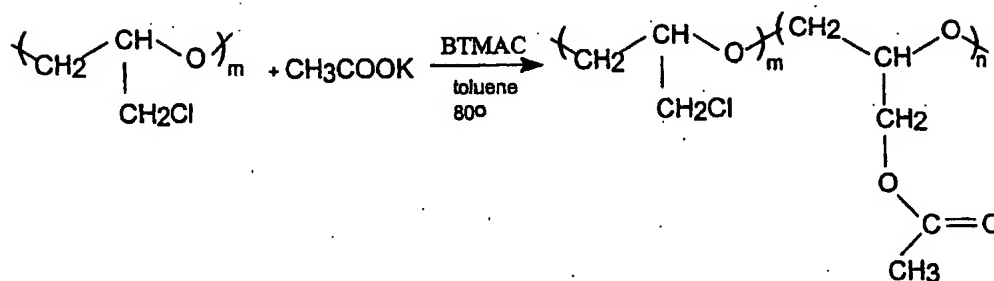
Figure 2. Modification of poly(epichlorohydrin) with acetate groups
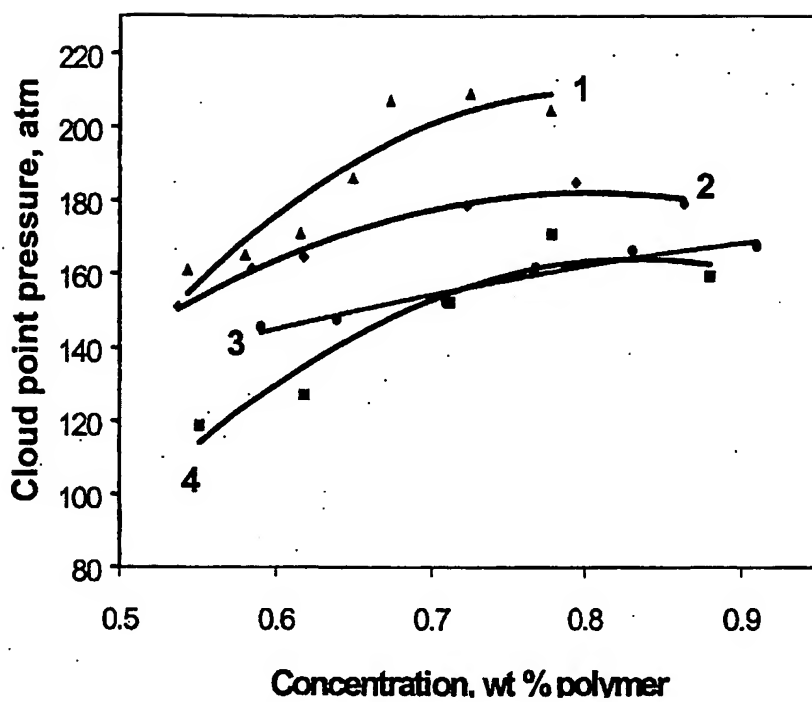
Figure 3.   Phase   behavior   of   acetate   functionalized

epichlorohydrin N = 25 repeat units

1) 33% acetate

2) 40 % acetate

3) PO homopolymer (also 25 repeat units)

4) 45 % acetate
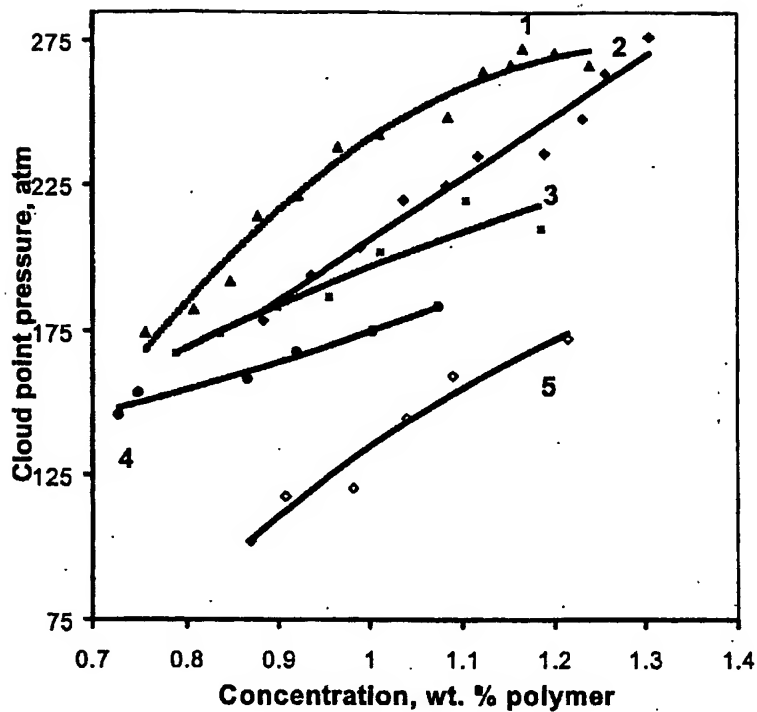
Figure 4. Phase behavior of acetate functionalized poly(epichlorohydrin) N = 7 repeat units

1) Epichlorohydrin homopolymer

2) 28 % acetate

3) 100 % acetate

4) 33 % acetate

5) 38 % acetate
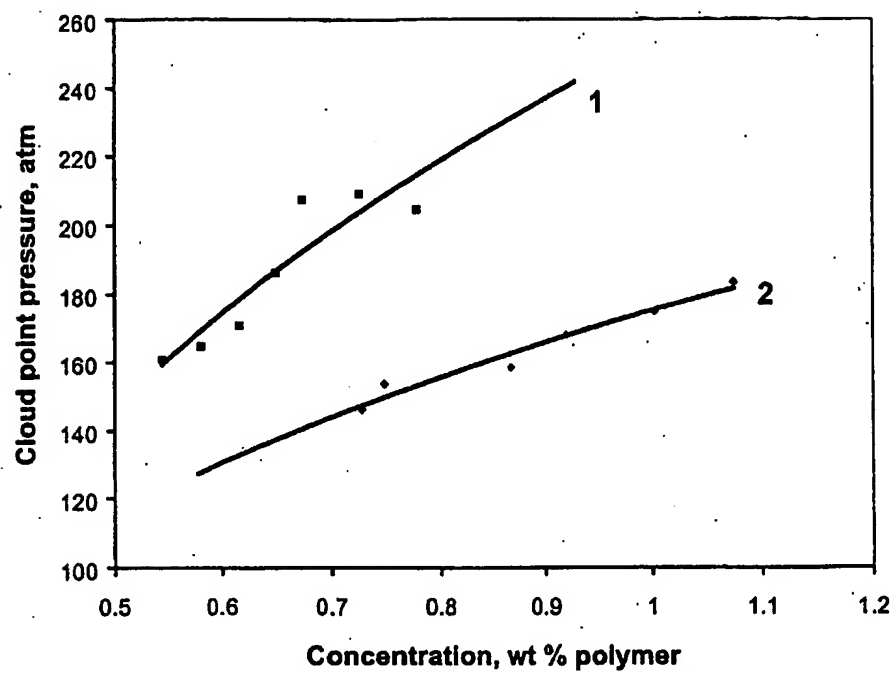
Figure 5. Phase behavior of functionalized poly(epichlorohydrin) with 33 % acetate

1) N = 25 repeat units

2) N = 7 repeat units
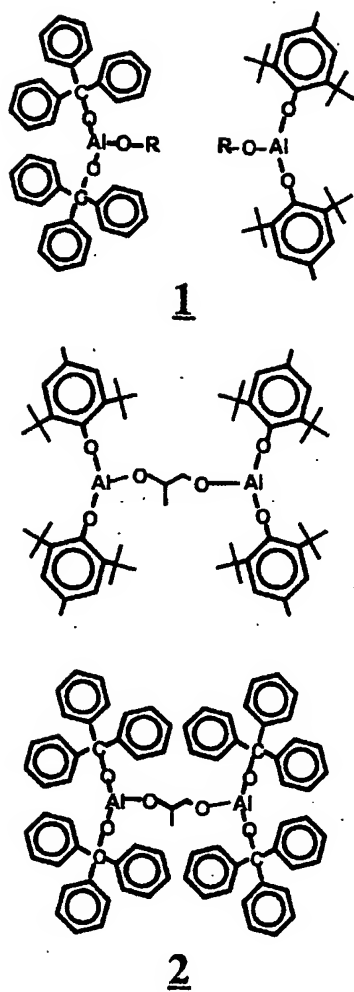
Figure 6. Sterically hindered aluminum catalysts used in the copolymerization of cyclic ethers and carbon dioxide

SYNTHESIS OF PO/CO₂COPOLYMERS
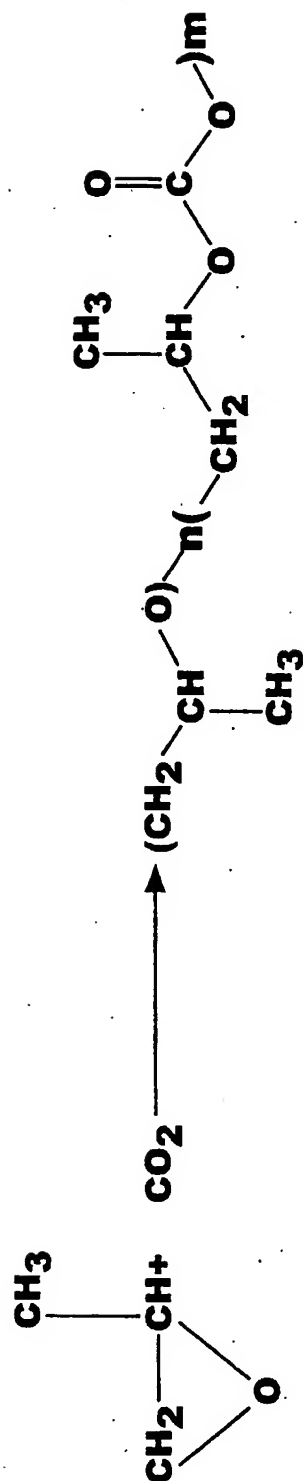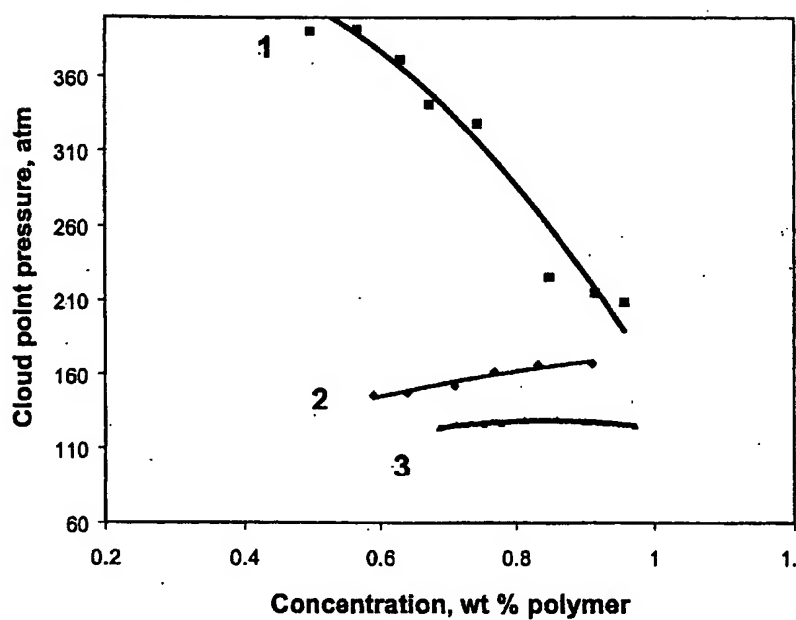
Figure 7

Figure 8. Phase behavior of PO-CO$_2$ copolymer with N = 25 repeat units

1) PO/CO$_2$ copolymer 56 % carbonate

5 2) PO homopolymer

3) PO/CO$_2$ copolymer 40% carbonate
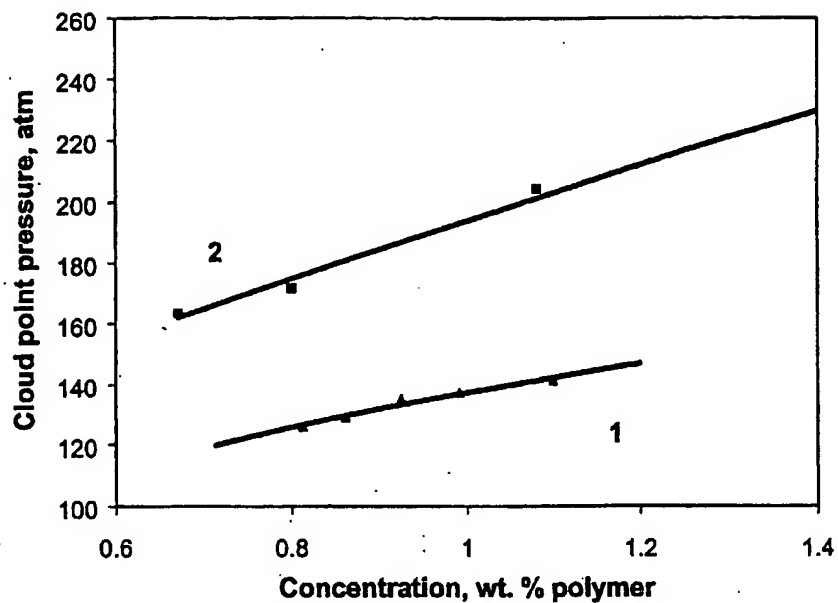
Figure 9. Phase behavior of PO-CO$_2$ copolymers vs. poly(fluoroether)

i) PO/CO$_2$ copolymer N = 220 repeat units, 15% carbonate

5   2) Krytox, N = 176 repeat units (reference 24)
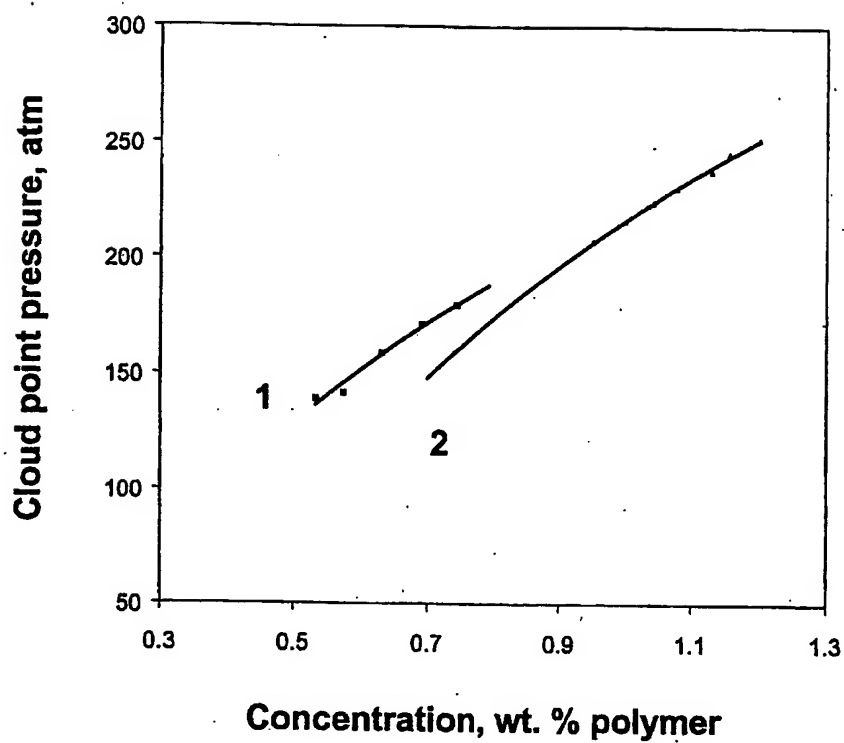
Figure 10. Phase behavior of EO-CO₂ copolymer vs. PEO

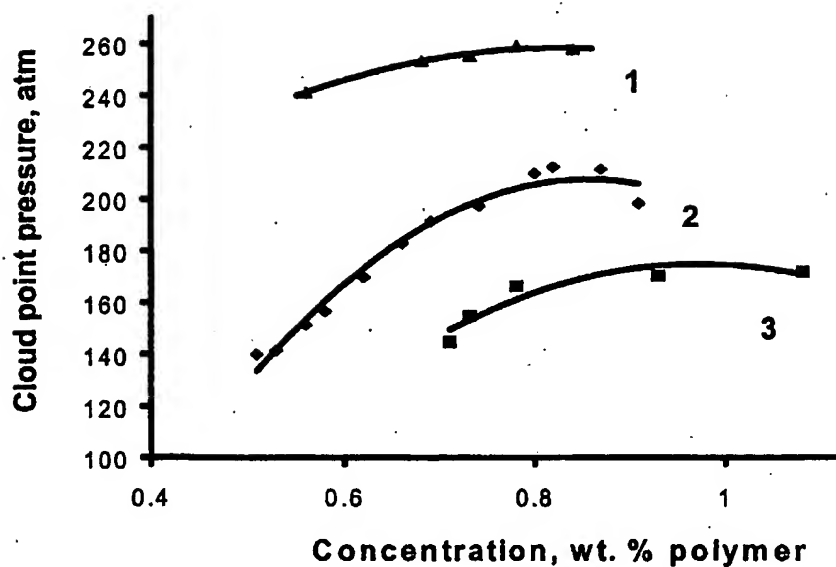1) EO/CO₂ copolymer N = 103; 33.7% carbonate

2) PEO, N = 16

Figure 11. Phase behavior of $CHO-CO_2$ copolymers with high content of carbonate units

1) 47% carbonate N = 27
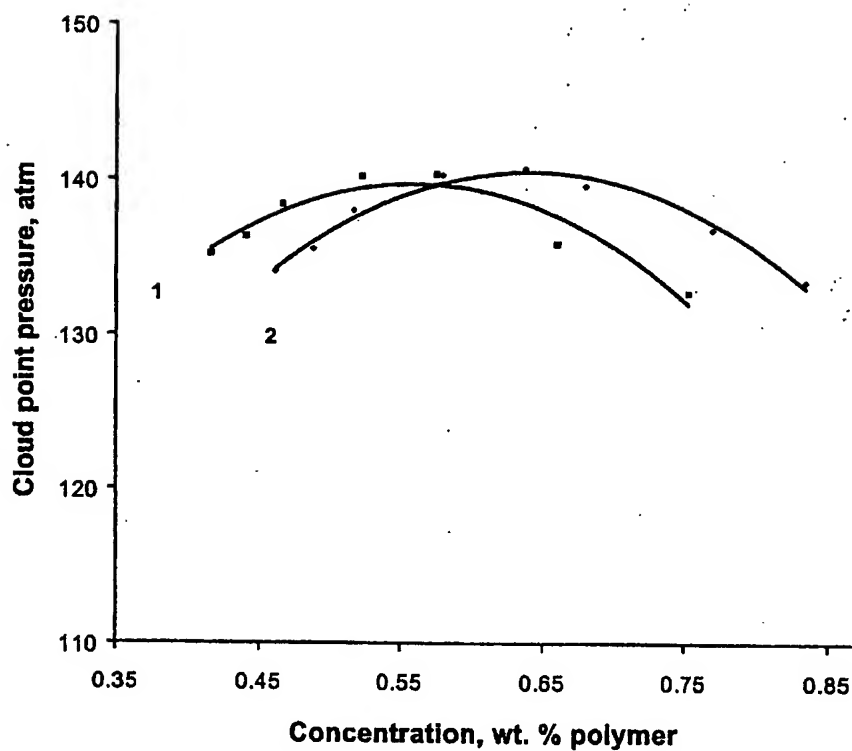
2) 40% carbonate N = 20

3) 50% carbonate N =16

Figure 12. Phase behavior of CHO-CO$_2$ copolymers with low content of carbonate units

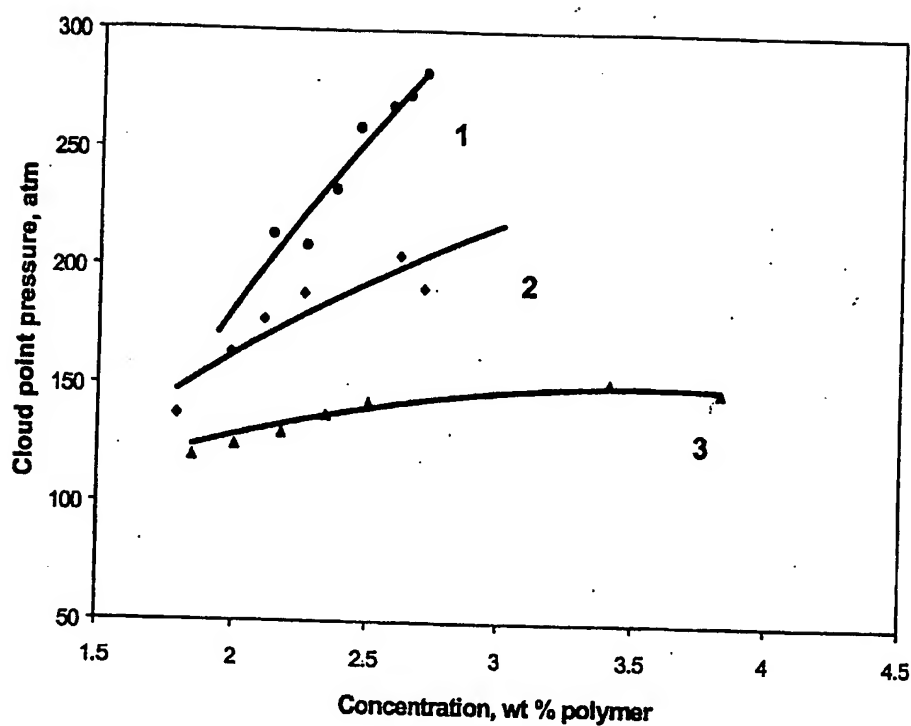1) 8.8% carbonate N = 124

5 2) 2.3% carbonate N = 88

Figure 13. Phase behavior of poly(propylene glycol) diol (1), poly(propylene glycol) monobutyl ether (2) and poly(propylene glycol) acetate (3) with 21 repeat units.
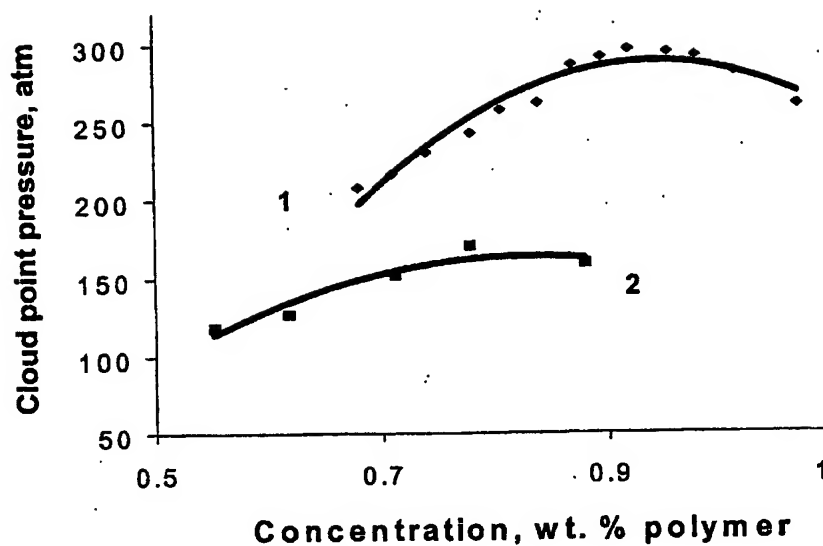
Figure 14. Phase behavior of epichlorohydrin/CO_2 copolymer compared to acetate modified poly(epichlorohydrin)

1) ECH/CO_2 copolymer
      N = 17

        25 % carbonate
2) Modified PECH
      N = 25
      45 % acetate

INTERNATIONAL SEARCH REPORT

A.	CLASSIFICATION OF SUBJECT MATTER

IPC(7)   :C07D 401/06
US CL   : 546/336
According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. :   546/336

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,872,257 A (BECKMAN et al.) 16 February 1999, col. 2, line 36 - col. 3 line 50.	1-62

☐ Further documents are listed in the continuation of Box C.　☐ See patent family annex.

	Special categories of cited documents:
"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier document published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed

"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 JANUARY 2001	01 FEB 2001

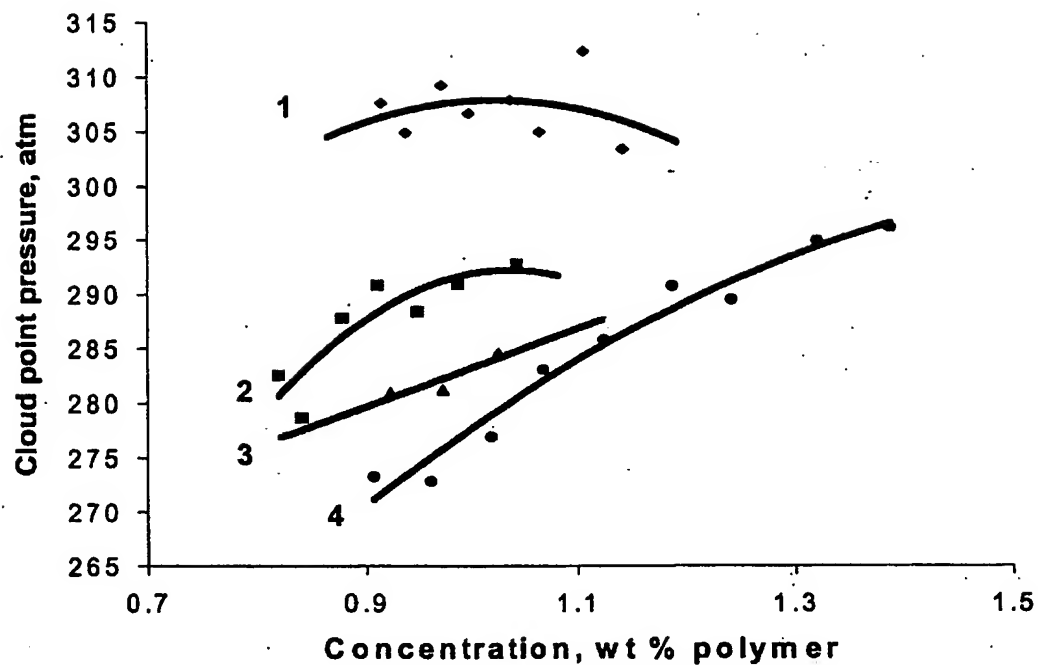| Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer TERRESSA BOYKIN Telephone No. (703) 308-0661	Jean Proctor Paralegal Specialist

Form PCT/ISA/210 (second sheet) (July 1998)*

5 **Figure 17.** Phase Behavior of Vinyl Acetate/Ethyl Vinyl

Ether Copolymers with 70 SRU

1) 67 % VA

2) 63 % VA
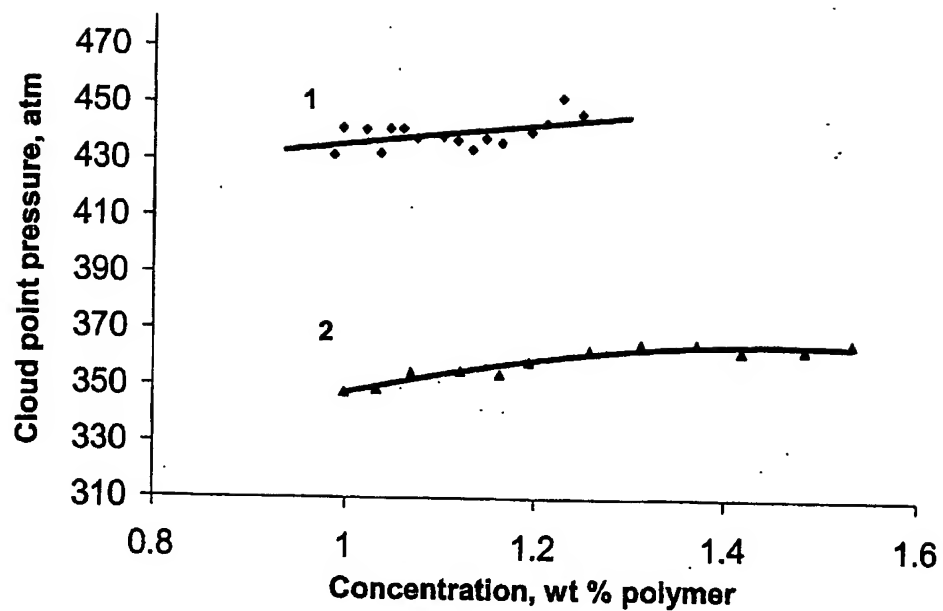
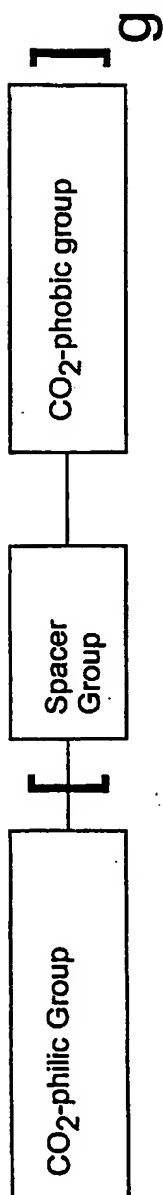3) VA homopolymer

10 4) 18.47 % VA

Figure 18. Phase Behavior of Vinyl Acetate/Ethyl Vinyl Ether Copolymers

1) 135 SRU, 46.6 % VA

2) 90 SRU, 39.8 % VA

(Reactive Functional Group)[(Monomer 1)$_x$(Monomer 2)$_y$](End Group)

Figure 19

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/26156

A. CLASSIFICATION OF SUBJECT MATTER
IPC(7)   :C07D 401/06
US CL : 546/336

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 546/336

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,872,257 A (BECKMAN et al.) 16 February 1999, col. 2, line 36 - col. 3 line 50.	1-62

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 JANUARY 2001	01 FEB 2001

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	TERRESSA BOYKIN Jean Proctor Paralegal Specialist
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0661

Form PCT/ISA/210 (second sheet) (July 1998)★